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Student Signature: Feng Wang

This work and its defense approved by:

Committee Chair: Anastasios Angelopoulos, PhD
Anastasios Angelopoulos, PhD

Marc Cahay, PhD
Marc Cahay, PhD

Vesselin Shanov, PhD
Vesselin Shanov, PhD

Junhang Dong, PhD
Junhang Dong, PhD

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Controlling the Hydrophilicity and Contact Resistance of Fuel Cell Bipolar Plate Surfaces Using Layered Nanoparticle Assembly

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By
Feng Wang

M.S. Polymer Science, East China University of Science and Technology, Shanghai, China, 2004
B.S. Polymer Science and Engineering, East China University of Science and Technology, Shanghai, China, 2001

Committee Chair: Dr. Anastasios P. Angelopoulos
Abstract

Hybrid nanostructured coatings exhibiting the combined properties of electrical conductivity and surface hydrophilicity were obtained by using Layer-by-Layer (LBL) assembly of cationic polymer, silica nanospheres, and carbon nanoplatelets. This work demonstrates that by controlling the nanoparticle zeta (ζ) potential through the suspension parameters (pH, organic solvent type and amount, and ionic content) as well as the assembly sequence, the nanostructure and composition of the coatings may be adjusted to optimize the desired properties.

Two types of silica nanospheres were evaluated as the hydrophilic component: X-Tec® 3408 from Nano-X Corporation, with a diameter of about 20 nm, and polishing silica from Electron Microscopy Supply, with diameter of about 65 nm. Graphite nanoplatelets with a thickness of 5~10nm (Aquadag® E from Acheson Industries) were used as electrically conductive filler. A cationic copolymer of acrylamide and a quaternary ammonium salt (Superfloc® C442 from Cytec Corporation) was used as the binder for the negatively charged nanoparticles. Coatings were applied to gold-coated stainless steel substrates presently used a bipolar plate material for proton exchange membrane (PEM) fuel cells.

Coating thickness was found to vary nearly linearly with the number of polymer-nanoparticle layers deposited while a monotonic increase in coating contact resistance was observed for all heterogeneous and pure silica coatings. Thickness increased if the difference in the oppositely charged ζ potentials of the adsorbing components was enhanced through alcohol addition. Interestingly, an opposite effect
was observed if the ζ potential difference was increased through pH variation. This previously undocumented difference in adsorption behavior is herein related to changes to the surface chemical heterogeneity of the nanoparticles.

Coating contact resistance and surface wettability were found to have a more subtle dependence on the assembly sequence and coating composition. Various LBL assembly sequences were investigated to control heterogeneous coating nanostructure and tune their hydrophilic and electrically conductive properties. Assembly from mixed nanoparticle suspensions yielded competitive nanoparticle adsorption and is denoted as cLBL assembly. The absence of intervening polymer binder during sequential deposition from first carbon then silica nanoparticle suspensions directed the assembly process with each applied layer and is denoted as dLBL assembly. Use of intervening polymer binder as in standard LBL deposition is denoted as sLBL assembly. The cLBL assembly sequence was found to yield nanoparticle competition for available surface sites between the heterogeneous nanoparticles and result in phase separation within each layer, producing coatings with high electrical contact resistance but poor hydrophilicity. Coatings prepared using dLBL assembly exhibited improved contact resistance due to improved alignment of a carbon phase perpendicular to the substrate surface but continued poor hydrophilicity. The sLBL assembly scheme produced optimum coating performance due to the adsorption of highly dispersed silica layers directly onto the graphite platelets, while maintaining through-plane platelet to platelet contact. The wetting behavior of the prepared coatings was satisfactorily described by Johnson-Dettre model while exhibiting little
response to changes in surface morphology (in contrast to Wenzel’s equation). Hydrophilicity of the cLBL assembled coatings could be enhanced by altering the silica nanoparticle ζ potential in mixed suspensions.

Coating durability was demonstrated through LBL assembly onto industrial-size bipolar plate materials and testing under PEM fuel cell operating conditions.
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Chapter 1. Introduction

1.1 Background

Fuel cells are expected to play a major role in the economy of the near future. It is anticipated that the hydrogen sustainable energy age would be ushered by the development of economical and reliable fuel cells. Many problems associated with environmental, economic, and energy security may be alleviated by fuel cells. Fuel cells are more efficient than other current technologies because they are electrochemical devices that can directly convert the chemical energy of a reaction into electrical energy, and because the moving parts are eliminated (meaning mechanically ideal). Because of a lack of moving parts, fuel cells are silent in operation. Furthermore, with hydrogen as the fuel, and the product being water, the process is very clean. These advantages suggest that fuel cells have the potential to reduce the problems associated with petroleum oil based energy production, including greenhouse-gas emissions, air pollution, etc. Moreover, unlike batteries, the scaling for fuel cells between power (which was determined by fuel cell size) and capacity (which was determined by fuel reservoir size) is independent. In fact, fuel cells combine many of the advantages of both combustion engines and batteries. Based on these numerous advantages, worlds’ governments, industries, and scientists have shown a lot interest in developing the fuel cells.

Unfortunately, fuel cells also have many disadvantages. High cost is the most serious disadvantage. Another significant limitation is power density. Fuel (H₂ for most cases) availability and storage pose further problems. Additional fuel cell
limitations include operational temperature compatibility, susceptibility to environmental poisons, and durability under start-stop cycling.

Due to the modestly low operation temperature, short start-up and transient-response times compared to other types of fuel cells that operated at higher temperatures (200 °C~1000 °C), polymer electrolyte membrane fuel cells (or Proton Exchange Membrane fuel cells) (PEMFC) are recognized by the U.S. Department of Energy (DOE) as the main candidates for future transportation applications\textsuperscript{11}. Higher-temperature fuel cells do not have the quick transient response behavior required for transportation propulsion, including start-up and shut-down\textsuperscript{5}. Moreover, power density for higher-temperature fuel cells is usually lower than PEM fuel cells.

1.2 Bipolar plates

Figure 1-1 shows the structure for PEM fuel cell and stack. An important part of the PEM fuel cell stack is the bipolar plates (BPs), currently which account for about 80% of the total weight and 45% of the stack cost\textsuperscript{12}. Many functions are expected to be accomplished by the BPs, such as distribute reactants over the active areas, remove heat from the active areas, carry current from cell to cell and prevent leakage of reactants and coolant\textsuperscript{13}. Many efforts are underway to develop the BP materials to satisfy these requirements. The materials investigated so far can be broadly classified as:
Figure 1-1. Schematic of PEM fuel cell and stack

Figure 1-2. Classification of materials for BPs used in PEM fuel cells
1. Non-metal: non-porous graphite/electrographite\textsuperscript{15}.

2. Metals: non-coated\textsuperscript{16} and coated\textsuperscript{17}.

3. Composites: polymer-carbon and polymer-metal\textsuperscript{18}.

Many reviews have appeared on the subject of BPs for PEM fuel cell\textsuperscript{13, 14, 19-21}. Figure 1-2 shows the detailed classification of BP materials. Usually, graphite composites are considered as the main material for PEM bipolar plates because of their excellent chemical stability and low resistivity. Unfortunately, their low mechanical strength and high manufacture cost block their application in the commercial market\textsuperscript{15}. Since durability and fabrication cost must be optimized to allow fuel cells to enter the commercial market and compete with other energy systems, much attention has been given to metallic bipolar plates. Compared with carbon-based materials, metallic materials have higher mechanical strength, better durability to shocks and vibration, little permeability to the reactants, better thermal conductivity and much superior manufacturability\textsuperscript{19}. However, the metal bipolar plates are more likely to corrode and dissolve\textsuperscript{22-25}. The corrosion layer on the BP surface increases the electrical resistance and decreases the output of the cell. The dissolved metal ions may cause the poisoning of the membrane and lead to considerable power degradation.

Based on these situations, considerable attempts are being made using noble metals\textsuperscript{17, 26}, stainless steel\textsuperscript{27-29} and various coated materials\textsuperscript{20, 30} to improve the corrosion resistance of the metals used without sacrificing too much surface contact resistance and maintaining cost effectiveness.

Surface energy and surface contact resistance of bipolar plates are two important
factors affecting cell performance since water produced by the cathode reaction should be immediately removed to avoid “flooding” \(^{31-35}\). Flooding occurs when water produced during the fuel cell reactions accumulates sufficient to obstruct the passage of reactant gases to the active sites of the fuel cell catalyst. High contact resistance of the bipolar plates will reduce voltage output due to partial conversion of chemical energy into heat energy. Bipolar plates with low surface energy could directly contribute to flooding of cathode side of the fuel cell by causing liquid holdup in the BP channels, as shown in Figure 1-3(b). To evaluate surface energy of different materials, the contact angle of water on the surface may be measured. Low contact angle is an indication of a high surface energy of a material and high surface wettability. In spite of numerous efforts to increase the conductivity and durability of BP’s, most of the bipolar plates researched so far have very low wettability (i.e. very high contact angle). The effect of surface energy for BPs on cell performance may be seen from Figure 1-3. The dramatically decrease of output voltage at high current density was attributed to mass transport effects. The mass transport effect can be ascribed to one or more of the following limitations\(^4\): reduced partial pressure of oxygen in air; limited diffusion of oxygen in the catalyst layer; and blocking of gas access by water droplets formed in the flow channel or inside the electrode. The increase of surface energy for BPs could let fuel cells work at higher current density by extending the current limitation, hence improve the cell performance.

The effect of surface contact resistance for BPs on fuel cell performance may be found from Figure 1-4. It may be seen that, the output voltage decreases when the
contact resistance increases at certain current density, resulting in more chemical energy transfer to thermal energy instead of useful electrical energy. Based on above

Figure 1-3. (a) Typical polarization curves for PEM fuel cell with different mass transport effect. Increase of surface energy for BPs could let fuel cells work at higher current density by extending the current limitation\textsuperscript{36}. (b) Liquid hold-up due to the hydrophobic surface, pressure drop will dramatically increase because of the hold-up\textsuperscript{37}.
At the same current density, the increase of contact resistance between BPs and diffusion media may decrease the voltage output of the fuel cell.

discussion, both contact resistance and contact angle must be as low as possible for best cell performance.

Table 1-1 shows the contact resistance and contact angle for some coated or uncoated bipolar plates with different coatings and bulk materials which are common to industry. It may be seen from the table that these two critical properties (i.e. low contact resistance and low contact angle) were difficult to achieve in any single material. For example, silica coating on gold owns low contact angle but high contact resistance; while epoxy/graphite composite could achieve low contact resistance but the contact angle for this material is very high. Furthermore, it also should be point out that simultaneous optimization of surface energy and surface contact resistance must occur while retaining the mechanical strength, thermal conductivity, durability
and low fabrication cost. Consequently, organic and inorganic coating materials can act as enablers to produce conductive, hydrophilic, and durable coatings for BPs.

Table 1-1 Contact resistance and water contact angle data for bipolar plates and coating materials common to industry

<table>
<thead>
<tr>
<th>Bulk Materials</th>
<th>Coatings</th>
<th>Contact Resistance</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite composite</td>
<td>/</td>
<td>21</td>
<td>86</td>
</tr>
<tr>
<td>316L SS (oxidation layer removed)</td>
<td>/</td>
<td>24</td>
<td>40</td>
</tr>
<tr>
<td>316L SS (with oxidation layer)</td>
<td>/</td>
<td>651</td>
<td>63</td>
</tr>
<tr>
<td>316L SS</td>
<td>TiN</td>
<td>40</td>
<td>90</td>
</tr>
<tr>
<td>316L SS</td>
<td>Polypyrrole</td>
<td>3459</td>
<td>70</td>
</tr>
<tr>
<td>316L SS</td>
<td>gold</td>
<td>20</td>
<td>84</td>
</tr>
<tr>
<td>316L SS/Gold</td>
<td>graphite</td>
<td>3.5 max</td>
<td>60</td>
</tr>
<tr>
<td>316L SS/Gold</td>
<td>silica</td>
<td>217 min</td>
<td>10</td>
</tr>
<tr>
<td>304 SS</td>
<td>CrN</td>
<td>9420</td>
<td>83</td>
</tr>
</tbody>
</table>

* the data without citation was obtained in our lab.

1.3 Layer-by-Layer (LBL) Assembly

The LBL assembly is a rich, versatile, and very inexpensive approach to thin film preparation via alternative adsorption of positively and negatively charged materials from aqueous solutions or suspensions. Iler 46,47 was the first to use this method to
deposit alternating layers of silica and alumina, with the incorporation of organic and inorganic nanoparticles into multilayer structures. Although this technique did not attract much attention right after its first investigation, the publications about LBL assembly increased exponentially in recent years (as seen in Figure 1-5). Since the work of Iler, numerous potential applications utilizing this approach have been investigated\textsuperscript{33, 43, 48-51, 51-75}. The most current trends for the LBL assembly may be found in the review papers\textsuperscript{73, 74}. This technique was successfully applied to the preparation of multilayer films for many different materials which may contain a number of different functional groups\textsuperscript{76, 77}, such as polymers\textsuperscript{70},

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/figure15.png}
\caption{Number of LBL papers published per calendar year}
\end{figure}

(data drawn from isi website source)
semitector, proteins, magnetic graphite oxides, dyes, clay platelets, and nanoparticles. Commerically, this approach has found wide acceptance in the electronics industry because of its simplicity and versatility.

Electrostatic LBL deposition involving polyelectrolytes and nanoparticle is one of the simplest and most cost-effective methods for preparing thin film for charged materials on solid substrates. The principle of electrostatic LBL assembly is based on spontaneous adsorption of oppositely charged polyelectrolytes and nanoparticles from their solutions or suspensions that take place if the free energy of adsorption, $\Delta G$, is negative and it is suitably to design and optimize the high-quality films with a defined composition on nanometer scale. Interfacial properties are very important in the preparation of advanced materials with specific and tailored functions. Compared with other method for surface modification such as spraying or rolling, the LBL approach offers a lot of key merits. An important advantage is that the layer thickness can be controlled precisely by varying (a) the specific materials being used, (b) the number of layers assembled, and (c) the specific adsorption conditions used. For example, by using variables such as assembled layer numbers, adsorption time, and the solvent polarity, the thickness of the multilayer can be controlled. A second advantage of LBL approach is that uniform films may be achieved even on the complex shapes, and is largely independent of the geometry of the surface. For instance, bipolar plates for proton exchange membrane fuel cell is one of the specific areas because of the ease of LBL method to eliminate the “shadowing effects”. The characteristics for the multilayer may be tuned with
relative ease by changing the adsorbed materials, adsorption conditions, and layer numbers.

1.4 LBL Assembly in Bipolar Plates

Many methods may be applied to coat the BPs surface. Dry coating application methods such as vapor phase deposition have been attempted\textsuperscript{93}, but are difficult to apply in practice because of “shadowing” effects resulting from the complex shapes of the BPs\textsuperscript{90}. Furthermore, dry process equipment is expensive to purchase and maintain. Conventional wet chemical coating application methods such as spray or rod application can solve these problems, but they cannot control the nanostructure of the coatings, which is necessary to optimize the performance of coatings. For example, the thin films prepared by the spraying method were less stable and much rougher than those prepared by the LBL approach\textsuperscript{91, 92}. An alternate approach is to employ the LBL self-assembly of organic polymers and inorganic nanoparticles on surfaces to create coatings nanostructures which could meet the stringent fuel cell requirement. This approach is the subject of the present proposal.

The self-organization of macromolecules and nanoparticles from liquid suspension onto solid surfaces has been employed to create assemblies with unique physico-chemical properties for many years. Specifically in PEM fuel cell fields, LBL self-assembly was used to from highly conductive and methanol resistance multilayers\textsuperscript{93}, polyelectrolyte membrane\textsuperscript{94}, bipolar plates\textsuperscript{52}, etc.

Recently, self-assembly of carbon nanoparticle multilayers has been investigated as
a coating method for BPs\textsuperscript{52} in our lab. The approach in these references involves the irreversible adsorption of alternating layers of positively charged polymers and negatively charged nanoparticles onto the surfaces. During the adsorption, the cationic polyacrylamide was firstly adsorbed onto the surface to form cationic layers. Then, the anionic layers consist of highly dispersed graphite nanoplatelets that irreversibly bind to the cationic polymer. The homogenous graphite multilayers had very low electrical contact resistance, demonstrating for the first time that the use of polymer binder during nanoparticle LBL assembly does not electrically insulate successively applied layers. For instance, the contact resistance for multilayers with 8 bilayers may be as low as 1.6 mΩ-cm\textsuperscript{2} at 200 psi and 1 A/cm\textsuperscript{2}. Unfortunately, these graphite multilayers are not sufficiently hydrophilic (water contact angle may be as high as 60º). The surface wettability of the thin films may be expected to be improved by the introduction of hydrophilic silica nanoparticles to form heterogeneous multilayers.

1.5. Objectives

It is desired to create hybrid coatings, which exhibit the properties of low electrical contact resistance, high wettability and good durability, by LBL technique on various solid substrates. It will be shown that by controlling the assembly conditions (pH, organic solvent content, assembly methods, adsorption time, etc), different types of functional coatings can be generated and LBL is a very versatile means to modify the functions including surface properties. The substrates of primary interest are electroplated gold on stainless steel and stainless steel. A key objective of the research
is to provide fundamental understanding of how non-covalent interactions (i.e. electrostatic, van der Waals forces, etc) among various components impact the three dimensional multilayer nanostructure and associated hydrophilicity and electrical conductivity. Another objective is to de-convolute the effects of surface chemistry from surface texture on surface wetting according to different theoretical models.

1.6 Approach

Electrostatic interactions between the nanoparticles and polymer are altered by varying the $\zeta$ potential of nanoparticles and polymers. In this research, a quantitative assessment of the extent of the electrostatic interaction between nanoparticles in a given suspending medium and subsequent to surface deposition is evaluated by $\zeta$ potential measurement. The relationship between $\zeta$, the nanoparticle surface charge, $\sigma$, and properties of the suspending media such as dielectric constant, $\varepsilon$, and ionic strength (as reflected in the Debye-Huckel parameter, $\kappa$), is given by the following expression:

$$\sigma = \frac{-2\kappa kT \varepsilon}{z e} \sinh \left( \frac{z e \zeta}{2kT} \right) \quad \text{(Equation 1-1)}$$

From this Equation, we may predict how to systematically modify nanoparticle interactions by altering suspending media compositions: (1) Debye parameter, $\kappa$, may varied by adding indifferent salt as well as changing the nanoparticle concentration, (2) dielectric constant, $\varepsilon$, may be varied through the addition of
alcohols, and (3) surface charge, $\sigma$, may be altered by varying the nanoparticle or polyelectrolyte synthesis procedure or, where surface charge results from the dissociation of functional groups, the pH of the suspending media. The influence of nanoparticle $\zeta$ on LBL adsorption behavior will be systematically examined in the present investigation.

In this thesis, various LBL assembly approaches will be used to obtain hydrophilic, electrical conductive, and durable thin films with homogenous or heterogeneous nanostructures on solid substrates for BPs application.

The first approach of multilayer self-assembly has been employed to create multiple bilayer structures as in Figure 1-6. In this approach, a cationic polyelectrolyte and anionic nanoparticles (silica) were employed alternately to form multilayer thin films with homogeneous structures. This approach is discussed in Chapter 3. Most of the LBL assembly research involved polymer and nanoparticles fall in this approach$^{43, 50, 62-68, 71, 72}$.

The second approach is to incorporate silica and graphite layers into the same multilayer structure, as shown in Figure 1-7, and was further investigated. As in the first approach, the cationic polymer was used as the binder for the two kinds of nanoparticles. After one polymer layer application, only one kind of nanoparticles was applied subsequently. The order of the silica and graphite particles was carefully adjusted to meet the requirements. Multilayers containing alternative nanoparticles prepared by LBL assembly, to our best knowledge, have not been explored extensively$^{69, 96, 97}$. 
Figure 1-6. Cross-section of self-assembled multilayer consisting of polymer and only one kind of nanoparticle

Figure 1-7. Schematic of multilayer cross-section formed using alternating bilayers of conductive and hydrophilic particles.

The last two approaches that will be investigated in this work are the co-deposition of colloid mixtures from suspension (e.g., simultaneous competitive assembly), and directed-assembly of silica nanoparticles onto the graphite-templated coating which was pre-assembled. The experimental procedures for these two methods will be discussed detailed in Chapter 4. The structures obtained by these two approaches are
depicted schematically in Figure 1-8. Research about directed-assembly has already extensively reported\textsuperscript{99-102}. However, multilayers containing nanoparticles prepared by directed-assembly have received little attention. Simultaneous competitive adsorption was been studied widely in polymer multilayers\textsuperscript{103}, biochemical\textsuperscript{104}, and gas adsorption filed \textsuperscript{105}, etc. In the present study, we reinvestigated the possibility of creating the nanoparticle multilayers by the competitive assembly method and demonstrated that coatings comprising two kinds of nanoparticles can be created by the aqueous based LBL technique.

\textbf{Figure 1-8. Schematic of multilayer cross-section formed with two different kinds of nanoparticles in the same layer}

Nanoparticles of different morphologies and adsorption kinetics are used to explore heterogeneous nanostructure formation with the previously described assembly schemes. Silica nanospheres will be shown in this thesis to reach adsorption equilibrium very rapidly within 1 minute, but 10 minutes is typically required in the case of the graphite nanoplatelets. Interactions between these nanoparticles and with
the polymer-coated substrate surface are varied by adjusting \( \zeta \) potential. \( \zeta \) potential is systematically varied by changing the solvent dielectrical constant, particle surface charge density, and ionic strength.

Nanostructure control is very important to the consequent coating properties. As will be discussed in detail next chapter, the water contact angle on chemically heterogeneous surfaces has been described by the Johnson-Dettre model. Johnson and Dettre have shown that for a chemically heterogeneous surface composed of domain sizes larger than molecular scale, the advancing and receding contact angles are indicative of the most hydrophobic and the most hydrophilic surface domains, respectively. On the other hand, the Johnson and Dettre model also predicts that as domain size decreases, sensitivity to surface chemical composition increases until the behavior approaches that of the Cassie equation at molecular scales. This observation indicates that contact angle may be hypothetically adjusted by controlling the multilayer assembly of heterogeneous nanoparticles on surfaces.

Contact angle is determined by the silica and graphite nano-scale domain distribution rather than the silica or graphite composition. On the other hand, coating conductivity is hypothesized to depend both on the conductive filler content (i.e. coating composition) as well as intralayer contact between the conductive (graphite) domains.
Chapter 2. Theory

As will be demonstrated in this chapter, the electrostatic forces between cationic polymers and negatively charged nanoparticles during LBL assembly and the stability of colloidal suspensions are related to the ζ potential of the various materials. Thus, fundamental knowledge about ζ potential behavior as a function of nanoparticle suspension formulation conditions, as will be discussed in this chapter, permits systematic alteration of these electrostatic forces. By adjusting these forces, the structure and properties of the prepared thin films may be controlled. Another key objective of this thesis is to de-convolute the effect of surface chemistry from that of surface texture on surface wetting behavior. Consequently the basic theories of surface wettability will also be reviewed in this chapter. Finally, since contact resistance of bipolar plates is another main factor that affects fuel cell performance, as discussed in Chapter 1, a description of the theory of electrical resistance measurement will be provided after the discussions of ζ potential and wettability theories.

2.1 Colloidal Suspensions Stability and Zeta Potential (ζ)

2.1.1 Colloids and ζ Potential Basics

Colloidal suspensions may be stabilized by various approaches\textsuperscript{106, 107}. The description of various stabilized methods comes from DLVO and non-DLVO theory. DVLO theory was developed by Derjaguin, Verwey, Landau and Overbeek in the 1940s. The classical DVLO theory involves van der Waals attraction and electrical
double-layer repulsion. The total interaction energy as a function of a separation distance between two particles may be obtained by the combination of these two forces \textsuperscript{108}. However, many experimental results could not be explained by solely DVLO theory \textsuperscript{109,110}. Thus, non-DLVO or structural forces describing the short-range forces are introduced. Non-DLVO theory involves the interactions from the adsorption of materials at the interface between the particles and liquid. Steric interactions, repulsive hydration interactions, and attractive hydrophobic interactions are the three categories for these non-DLVO interaction forces \textsuperscript{111}.

In this thesis, the colloidal suspensions stability was primarily rely on electrostatic repulsion between the nanoparticles (i.e. fall in DLVO theory). More importantly, electrostatic attraction forces between the positively charged polymer and negatively charged nanoparticles also play a critical role in LBL assembly. \( \zeta \) potential is an important variable for estimating the electrostatic interaction among particles and between particles and polymers, and it arises from the positively or negatively charged particles or charged polymer coils in liquid media.

Most colloidal dispersions in liquid media carry an electrical charge because of the dissociation of functional groups of particles or association of charged ions on the particle surface. The distribution of ions in the surrounding interfacial region may be affected by the net charge at the particle surface, i.e., an increased concentration of counter ions close to the surface would occur. Thus, each charged particle is surrounded by an electrical double layer. The liquid layer surrounding the particle is traditionally divided into two parts; an inner region, named Stern layer, where the ions
are strongly bound to the particle, and an outer region, called Diffuse Layer, where ions are less firmly associated onto the particle surface. Within the diffuse layer, there is a notional boundary inside which the ions and particle form a stable entity. Ions within the boundary move when the particle moves (e.g. due to gravity or electrical field), while those ions beyond the boundary stay with the bulk liquid. The potential at this boundary is called ζ potential, seen in Figure 2-1.

Figure 2-1. Schematic of ζ potential and electrical double layer around the charged particle

Gouy-Chapman theory is widely used to obtain the relationship between ζ potential and the nanoparticle surface charge (σ).
\[
\sigma = \frac{-2\kappa KT\varepsilon}{ze} \sinh \left( \frac{ze\zeta}{2KT} \right) \quad \text{(Equation 1-1)}
\]

As mentioned in Chapter 1, where \( \varepsilon \) is the suspending media dielectric constant, \( \kappa \) is called Debye-Huckel parameter which reflected ionic strength, \( K \) is Boltzmann’s constant, \( T \) is the absolute temperature, \( e \) is the electron charge, and only a symmetric electrolyte is considered such that the charge \( z = z^- = z^+ \).

Equation 1-1 shows how \( \zeta \) potential may be adjusted by changing various suspension parameters. However, application of this equation is not straight forward. The Debye parameter, \( \kappa \), for all suspensions investigated in this study has a value >0.5nm\(^{-1}\) and the measured particle radius, \( a \), has a value about 20nm (consequently, \( ka >10 \) and the double layer is thin relative to the particle radius), Consequently, equation 1-1 may be simplified to that is known as the Debye-Huckel approximation:\(^95\)

\[
\zeta = -\frac{\sigma}{\varepsilon\kappa} \quad \text{(Equation 2-1)}
\]

Thus, \( \zeta \) is inversely proportional to \( \kappa \) and \( \varepsilon \) and directly proportional to \( \sigma \).

### 2.1.2 How to Measure \( \zeta \) potential Experimentally

Although surface charge is difficult to obtain, \( \zeta \) potential may be measured using electrophoretic mobility. The mobility may be easily measured using dynamic light scattering and application of the Smoluchowski Equation (Equation 2-2) when
\( \kappa a \gg 1 \). 

\[ u_E = \frac{\varepsilon \zeta}{\eta} \]  

(Equation 2-2)

Where \( u_E \) is the particle mobility, \( \eta \) is the viscosity, \( a \) is the particle radius.

In general, Henry’s equation\(^{112} \) applied

\[ u_E = \frac{2 \varepsilon \zeta}{3 \eta} f(\kappa a, \zeta) \]  

(Equation 2-3)

Where the function \( f(\kappa a, \zeta) \) is affected by the particle shape, electrolyte types, etc.

### 2.1.3 Factors Affecting \( \zeta \) potential

There are many factors which could affect \( \zeta \) potential magnitude, such as pH, ionic strength, solvents, temperature, etc.

The pH of the liquid media is one of the most important factors that affects the \( \zeta \) potential of particles through its effect on \( \sigma \). A typical \( \zeta \) plot versus suspension pH may be found in Figure 2-2 generated using data to be discussed later in this thesis. It may be seen that the acidic particles tend to acquire more negative potential if more alkali is added to the suspension. If acid is added to the suspension, the \( \zeta \) potential is less negative. Further addition of acid results in a point where the charge will be neutralized. Potential may be positive if even more acid is added. The point where the particle \( \zeta \) potential becomes zero is named isoelectric point (IEP). IEP is very important parameter in colloidal science, as nanoparticle suspensions tend not to be stable in this region.
Ionic strength may be altered by the addition of salt. Inorganic ions can interact with charged particle surfaces by two different ways\textsuperscript{112}, (i) non-specific ion adsorption, which do not effect the isoelectric point. (ii) specific ion adsorption, which would cause a change in the value of the isoelectric point. Sometimes the addition of ions is even very little, it could have a dramatic effect on the $\zeta$ potential. In some cases, it can even lead to charge reversal of the surface. For example, while at very high ionic strength (take Na$^+$ for instance), the negative charged silica particles could convert to be positive by the adsorption of ions\textsuperscript{114}.

\[
\equiv SiOH + Na^+ \rightarrow SiOHNa^+ \quad \text{instead of} \quad \equiv SiOH \rightarrow SiO^- + H^+
\]
Generally speaking, the increase of ionic strength would decrease the absolute values of ζ potential (i.e. negative becomes less negative, and positive becomes less positive). According to Equation 1-1, the increase of κ due to the addition of ions may decrease |ζ| if surface charge (σ) was not changed. Numerous experimental results are consistent with this conclusion.112, 114-116.

Solvent chemistry can affect the magnitude of ζ potential in complicated ways. Specific solvent surface adsorption or solvent dissociation can alter the surface charge. Also, the dielectric constant of the solvent can affect the potential decay profile from the surface to bulk suspension in direct and indirect ways (by impacting solubility and dissociation constant of ionic species).114,116, 117 If organic solvent is added into the colloidal suspensions, the effects are two fold. One is that the dielectric constant would be decreased by the addition of the solvent,117, 118 the other is that the surface charge might be affected the adsorption of organic molecules onto the particle surface.114

Because the dielectric constant and ionic product of solvents are temperature dependent,114, 119 the ζ potential can vary when temperature changed. Previous research120, 121 has shown that the negative surface charge of silica at given pH and ionic strength increases when the temperature increases.
2.2 Wettability

2.2.1 Basics for Contact Angles

Wetting behavior is very helpful to understand the interfacial interactions between liquid, solid and vapor. Contact angle (θ) is used as an indicator for wettability. A low contact angle means high hydrophilicity and high surface energy for the surface. Figure 2-3 shows a schematic diagram for a sessile liquid drop on the solid surface.

![Figure 2-3. Sessile liquid drop on a solid surface. Where θ is the contact angle, γ_{SV}, γ_{SL} and γ_{LV} are the interfacial tensions which occurred at the solid-vapor, solid-liquid, and liquid-vapor interface, respectively.](image)

When the drop reaches equilibrium on a surface, the contact angle may be obtained by the following Young’s law

\[ \cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \]  

(Equation 2-4)

Currently, two main techniques are usually used to measure the contact angle. One is called the sessile drop method and the other is named Wilhelmy plate method. In the sessile drop method, a drop of liquid is applied to a horizontal surface and the edge is observed through a telescope, as seen from Figure 2-3. Two main advantages
of the sessile drop technique are speed and convenience\textsuperscript{123}.

Figure 2-4. Schematic of Wilhelmy Plate experiment showing contact angle hysteresis.

The typical Wilhelmy Plate Method is depicted schematically in Figure 2-4. Advancing contact angle is the angle ($\theta$), when the sample plate is immersed into the liquid, at the three-phase contact line obtained by measuring the force ($F$) exerted on the sample. Receding contact angle is the obtained angle when the sample plate is pulled out from the probe liquid. Usually, the advancing contact angle is larger than the receding contact angle. Contact angle hysteresis is the difference between the observed advancing contact angle and the observed receding contact angle. The
reason for contact angle hysteresis may be attributed to the existence of many thermodynamic metastable states for system having three-phase boundaries. Each contact angle is associated with a different metastable state. Advancing angle is referred for the maximum stable angle, and receding angle is for the minimum stable angle. The relationship between contact angle ($\theta$) and force ($F$) may be expressed by the following Equation 124, 125:

$$F = l\gamma \cos \theta$$  \hspace{1cm} (Equation 2-5)

Where $l$ is the perimeter for the sample plate, $\gamma$ is the surface tension of the liquid. Compared with the sessile drop method, the advantages of the Wilhelmy plate method included 123: (1) the personal effect of the measurement may be minimized; (2) it is independent to the liquid drop size; (3) the sensitivity of this technique is very high.

2.2.2 Effects of Chemical Composition on Contact Angles

The wetting behavior or contact angle of a surface is determined by its surface chemical composition, chemical phase distribution, and micro or nanotexture. The correlations of contact angle related to chemical distribution were developed by the thermodynamic analyses of Johnson and Dettre a number of years ago126, and this behavior has been discussed in significant detail127-130. The impact of morphology and composition on wetting behavior has also been described by Wenzel 131 and Cassie132.
Figure 2-5. Contact angle hysteresis as a function of surface composition. The upper curve corresponds to the advancing angle, and lower curve to the receding angle. The X axis is the fraction of the surface covered with low contact angle material, and the Y axis is the contact angle. Liquid contact angles: $\theta_1 = 120^\circ$, $\theta_2 = 0^\circ$. 1, 2, 3, 4 are referred to energy barrier height. Drop volume was 0.05ml\textsuperscript{126}.

Figure 2-6. (a) Two areas with a higher contact angle outside the contact line will impede advancement, leading to a higher advancing contact angle. (b) An area of a lower contact angle within the contact line will impede recession, causing a lower receding contact angle\textsuperscript{133}. 
A clear schematic description for Johnson-Dettre model for contact angle hysteresis was reported in the literature\textsuperscript{126,133}, and is shown in Figure 2-5. In the report\textsuperscript{126}, Johnson and Dettre analyzed the water contact angle behaviors on a model heterogeneous surface made of concentric circular bands. The contact angle hysteresis which is observed on nearly all solid surfaces may be explained by the key finding of Johnson and Dettre analyses. Briefly, the advancing and receding contact angles are indicative of the most hydrophobic and the most hydrophilic surface domains for a chemically heterogeneous surface composed of domain sizes larger than molecular scale. That is, for sufficiently large surface domains, dynamic macroscopic wetting behavior is insensitive to surface chemical composition except for surfaces that are nearly homogeneous. Moreover, as domain size decreases, sensitivity to surface chemical composition increases until the behavior approaches that of the Cassie Equation at molecular scales\textsuperscript{134}. The curve, labeled $A$ in the Figure 2-5, is calculated by the Cassie Equation\textsuperscript{134}:

$$\cos \theta' = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad \text{(Equation 2-6)}$$

Where $\theta'$ is the water contact angle on the heterogeneous surface, $f_1$ and $f_2$ are the surface fraction of the two components, $(f_1 + f_2 = 1)$, $\theta_1$ and $\theta_2$ are the water contact angle on each components.

Thus, systematic control over surface chemical domain size will permit systematic control over surface wetting.
2.2.3 Effects of Surface Roughness on Contact Angles

The apparent contact angle of a liquid on the surface also depends on the roughness of the surface. It is well known that increase of surface roughness of the solid may amplify the wetting properties. In another word, hydrophilicity may be increased by increasing the roughness of a hydrophilic surface, and hydrophobicity may be increased by increasing the roughness of a hydrophobic surface. Roughness changes the surface free energy at the solid interface but it does not change the liquid-vapor contribution. The relationship between contact angle and roughness may be expressed by the followed Wenzel function:

\[
\cos \theta' = r \cos \theta
\]

(Equation 2-7)

Where \( \theta' \) is the observed water contact angle on a rough surface, \( \theta \) is the intrinsic contact angle as measured on a smooth surface with the same material, and \( r \) is the surface roughness which is defined as the ratio of the actual surface area over its geometric surface area.

Although Cassie and Wenzel Equations are consistent with many observed results for numerous surfaces that have been studied in the last fifty years, some examples of where they are not consistent have also been reported. More complex models for rough and composition surfaces have also been reported.

2.3 Contact Resistance

As an indicator of electrical conductivity, contact resistance was measured by a custom built hand-press from Carver Company. Gold coated platens were attached to
a swivel point on the press and connected to a power supply. Teflon tape on one platen surface defines a 1 inch$^2$ contact area into which was placed a 1 inch$^2$ coated sample. During measurement, the sample is sandwiched between two graphite sheets, which acted as carbon diffusion media in PEM fuel cells. This method was used widely to measure the electrical contact resistance in PEM fuel cells$^{144,145}$. Figure 2-7 showed the schematic for the contact resistance measurement, and Figure 2-8 is the photo for the instrument used during the research.

During the measurement, a contact pressure of 200 psi and a current density of 1A/cm$^2$ (6.5Amps) were applied. The potential drop (V) between the two gold coated platens was recorded, and then resistance ($R'_c$) may be obtained from the following Equation with the unit of $\Omega - cm^2$.

$$
R'_c = \frac{V}{A} = \frac{V}{1A/cm^2}
$$  \hspace{1cm} (Equation 2-8)

It was worth to mention that $R'_c$ depends on several resistances in series, including the resistance for two gold platens, two carbon paper layers, the bulk resistance of the specimen, and more significantly, the contact resistance between the carbon papers and gold platens, and between the carbon papers and the specimen. To obtain the contact resistance for coated specimen, the calibration method was used to separately measure the value of coated specimens ($V'_1$) and the resistance of the uncoated bare substrate($V'_2$). Then the coating contact resistance may be obtained by,
Figure 2-7. Schematic for the contact resistance measurement

Figure 2-8 Photo of the instrument for contact resistance measurement
The number 2 was used in the above equation because both sides of the specimens were coated.

The through plane volume electrical resistivity, $\rho$, of the coating may be obtained from this contact resistance and the estimated thickness, $t$, of the coating using

$$\rho = \frac{R_c}{t}$$

(Equation 2-10)

Where the coating surface is assuming to conform perfectly to the electrode surfaces. Since this is unlikely in the case of LBL assembled nanoparticle coatings, Equation 2-10 provides only an upper bound on the volume resistivity in the present study.

The thickness, $t$, for a given LBL assembled coating was obtained from EDS data using Monte-Carlo electron flight simulations under the same microscope conditions as these used experimentally. How to obtain the coating thickness will be discussed in detail in the experimental and result chapters. The unit for $\rho$ is then $\Omega \cdot cm$.

Instead of contact resistance, electrical conductivity, $\sigma$, with the unit of $S/cm$ was also commonly used in some study. The relationship between $\sigma$ and $\rho$ is

$$\sigma = \frac{1}{\rho}.$$
Chapter 3  Experimental

3.1 Materials

3.1.1 Silica Nanoparticles

Two types of silica nanoparticles were obtained for this study from commercial sources. NanoX silica was obtained with a solids content of 5% by weight in a 20% by volume ethanol in water base, which is known as X-TEC 3408 (NanoX) and is available from NanoX Corporation. It has a reported average particle size of 19 nm in diameter. Polishing silica (EMS), purchased from Electron Microscopy Sciences, was obtained in an alkaline (NH₄OH) base at 40% solids content with a reported average particle size of 65 nm. Particle size will be confirmed utilizing photon correlation Spectroscopy (PCS or dynamic light scattering) as will be described later.

Figure 3-1 shows the surface groups for the silica particles. The anionic surface charge on the silica nanoparticles arises from the dissociation of weakly acidic silanol groups. Because the dissociation degree is related to pH of suspension, the effect of pH in both the anionic silica suspension and the corresponding cationic binder solution on multilayer formation is expected to play an important role in LBL assembly. In addition, the dielectric constant of the suspending medium is altered by the addition of ethanol in varying amounts. From Equation 2-2 \( \left( u_{E} \propto \frac{\varepsilon \zeta}{\eta} \right) \), the dielectric constant and viscosity of the solvent is necessary for the determination of the \( \zeta \) potential via the Smoluchowski method. The effect of ethanol and iso- propanol content on various solution properties is shown in Table 3-1 and 3-2, respectively.
Dielectric constants for solvents with varying ethanol content were obtained experimentally using a dielectric constant meter from Brookhaven Instruments (model BI-870) and are compared to literature values\textsuperscript{146}. The refractive indexes and viscosity employed for light scattering measurement are also shown in Table 3-1 and Table 3-2. Such alteration will permit systematical variation of the \( \zeta \) potential and subsequent nanoparticle interaction with both the pre-adsorbed cationic binder as well as with the cationic binder in solution after the cationic nanoparticles have been deposited.

Anionic silica suspensions were prepared by mixing desired amount of raw suspension in prepared solvent (including alcohol) and adding \( \text{H}_2\text{SO}_4 \) (ACS Plus Grade, Fisher Scientific) to maintain the desired pH.

![Figure 3-1. The surface groups on the edges of the silica layer](image-url)
### Table 3-1. Effect of Ethanol Content in Aqueous Solution

<table>
<thead>
<tr>
<th>properties</th>
<th>Ethanol Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>Refractive index (from ref ¹⁴⁷)</td>
<td>1.33</td>
</tr>
<tr>
<td>dielectric constant (measured)</td>
<td>80.8</td>
</tr>
<tr>
<td>dielectric constant (from ref ¹⁴⁶)</td>
<td>80.4</td>
</tr>
<tr>
<td>viscosity (cp) (from ref ¹⁴⁸)</td>
<td>0.89</td>
</tr>
</tbody>
</table>

### Table 3-2. Effect of IPA Content in Aqueous Solution

<table>
<thead>
<tr>
<th>properties</th>
<th>IPA Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>Refractive index (from ref ¹⁴⁹)</td>
<td>1.33</td>
</tr>
<tr>
<td>dielectric constant</td>
<td>80.4</td>
</tr>
<tr>
<td>viscosity (cp) (from ref ¹⁵⁰)</td>
<td>0.89</td>
</tr>
</tbody>
</table>

#### 3.1.2 Graphite Platelets

The fine graphite platelets, obtained from Ladd laboratories, are available commercially as an alkaline paste known as Aquadag-E, which is employed extensively as an electrically conductive coating in cathode ray tubes. Although this material is traditionally applied in the form of a paste, these graphite platelets are found able to form stable suspensions at the appropriate pH⁴³.
Figure 3-2 High resolution TEM image for graphite platelet.

Figure 3-3. Possible structure of oxygen complex on carbon surface. (a). carboxyl group, (b). carboxylic anhydride, (c). lactone, (d). lactol, (e). phenolic hydroxyl group, (f). carbonyl group, (g). o-quinone-like structure, (h). ether-type oxygen. The groups (a) to (e) have acidic properties.
The graphite platelets have previously been extensively characterized in our lab⁴³. For brief summary, the graphite platelets are composed of stacked graphene sheets to a total thickness of between 5 and 10 nm, as shown in Figure 3-2. The graphite platelets have high polydispersity in other dimensions, with the flat size ranging from 0.2 to 1.7 microns.

Our pervious XPS results showed that about 5% of the graphite surface was oxidized⁴³, and the oxidized graphite having both acidic and basic functional groups is responsible for a surface charge on the particle with sign and density that depends on the pH of the solution. A negative charge arises from the dissociation of acidic surface oxygen complex such as carboxylic and phenolic groups. The positive surface charge, its principle is still under investigation, may be attributed to the basic groups like pyrones or chromenes, or to the electron rich regions within the grapheme layers¹⁵². Furthermore, the decrease in oxygen content will cause the increase in its hydrophobicity. Figure 3-3 shows some groups on the carbon surface. Although the surface groups of the carbon nanoparticles are very complicated, these natures may be helpful to alter the multilayer architectures and wetting, and it will be demonstrated in this thesis.

3.1.3 Cationic Polymer

The cationic binder that will be employed in this study is a random copolymer of acrylamide and a quaternary ammonium salt (acrylamide/β-methacryl-oxyethyl-trimethyl-ammonium random copolymer). The schematic of the cationic polyacrylamide is shown in Figure 3-4. This specific material, obtained from Cytec
Corporation and commercially known as Superfloc C442, has a charge density of 10%. This is a strong polyelectrolyte with a constant cationic charge density which is independent of solution pH when the solution pH is below 8. The cationic binder has been described and extensively characterized in detail in previous investigations\textsuperscript{43, 50, 51}. The pH of all suspensions was maintained at a value sufficiently low to prevent dissociation of the hydrolyzed acrylamide groups on the cationic binder (onset at pH 8) while maintaining a strong negative charge in the colloid suspension for stabilization. \( \zeta \) potential measurements as a function of pH for this cationic polymer were shown in Figure 3-5. A positive \( \zeta \) potential was obtained at all pH values investigated, with the magnitude increasing from a value of 7 mV at pH 1 to a maximum value of 29 mV at pH 5. Such an increase is consistent with the decrease of ionic strength in the solution since pH 1 contains more ions than pH 5. A decrease in \( \zeta \) potential is observed when the pH increases from 5 to 7. Such a decrease is consistent with the onset of carboxylic acid group dissociation and the presence of amphiphilic groups along the polymer chain\textsuperscript{50}.

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 \\
(CH_2)_m & \quad (CH_2)_n \\
\cdots & \quad \cdots \\
\text{C=O} & \quad \text{C=O} \\
\text{NH}_2 & \quad \text{O} \\
\text{(CH}_2\text{)}_2 & \quad \text{N(\text{CH}_3)}_3 \\
\text{(CH}_3\text{)}_4 & \quad \text{CH}_3\text{SO}_4
\end{align*}
\]

Figure 3-4 Structure of the polyelectrolyte used as cationic binder in LBL formation, The \( x/y \) ratio was \( \sim 0.1 \).
Cationic polymer is used as a binder in the multilayer formation. The adsorption amount of nanoparticles is somewhat related to the polymer adsorption amount or surface coverage, so it is necessary to obtain the polymer surface coverage. Without cationic polymer, the negatively nanoparticles were found unable to absorb onto the substrates. Previous analysis of XPS data has indicated that the polymer adsorbs in a flat, all train conformation under similar experimental conditions. The surface coverage may be achieved by applying Cassie relationship:

\[
f = \frac{W - W_s}{W_a - W_s} \quad \text{(Equation 3-1)}
\]

Where \( f \) is the polymer surface coverage, \( W \), \( W_s \), and \( W_a \) are adhesion work of water on polymer covered surface, on bare substrate surface, and on polymer
surface, respectively.

The adhesion work may be obtained by the following Young-Dupre function $W = \gamma_{lv}(1 + \cos \theta)$ (Equation 3-2)

Where $\gamma_{lv}$ is water surface tension ($72.8 \text{mN/m}$), $\theta$ is the water contact angle. The water contact angle for different surface may be found in Table 3-3. The water contact angle for cationic polyacrylamide is zero because this polymer is very highly water soluble.

**Table 3-3 Contact angle of water on different surface**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Advancing Water contact angle(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare gold substrate</td>
<td>84.4</td>
</tr>
<tr>
<td>cationic polyacrylamide</td>
<td>0</td>
</tr>
<tr>
<td>Substrate coated with polymer</td>
<td>49.4</td>
</tr>
</tbody>
</table>

* the polymer solution has a concentration of 0.13g/l with pH 4.6, the coating time is 2 min. There is only one layer of polymer coated on the substrate.

Under the experimental conditions shown below table 3-3, the polymer surface coverage is about 61.3%. This result is consistent with previous investigations of cationic polyacrylamide adsorption $^{153}$.

**3.1.4 Substrates**

The substrate material used in multilayer formation is electroplated gold with 200
nm thickness on 316 L stainless. These substrates are employed as a main candidate material for bipolar plate in fuel cell applications and were kindly supplied by the General Motors Corporation (GM). Irreversible adsorption of the cationic polyacrylamide to be employed in this study has been previously observed on various substrate surfaces, including electroplated gold. As will be described shortly, another advantage for the use of gold as the substrate material is that it permits accurate assessment of the resistivity of the deposited layers. Substrates were cut into 1 inch × 1 inch squares and then cleaned with methanol (Fischer Scientific, ACS Spectrophotometric Grade) and a lint-free cloth to remove any fingerprints prior to coating application.

The wettability for the bare gold substrate surface may be obtained from Table 3-3, i.e. the advancing contact angle of water is about 85º. The relationship between contact resistance and pressure for the uncoated electroplated gold was investigated before the measurement of contact resistance for coated samples, as shown in Figure 3-6. It may be seen that the contact resistance dropped significantly with the increase of pressure when the pressure was below 150psi, and then was level off. In present study, the pressure chosen is 200psi, a value around which the contact resistance only changes slightly with the pressure, and this pressure is also chosen for PEM fuel cell industry to install the stacks.

3.1.5 Other Materials

Other main materials include H₂SO₄ (Fisher Scientific, ACS Plus Grade), NaOH (Fisher Scientific, Certified ACS grade), ethanol (Fisher Scientific, ACS
De-ionized (DI) water is obtained by passing a 1 MΩ resistivity house water supply through a Millipore Synthesis water purification unit to achieve 18.2 MΩ.

Figure 3-6. The relationship between contact resistance and pressure for gold substrate.

3.2 Nanoparticle Suspension and Polymer Solution Formulation

3.2.1 Silica Suspensions

Preparation of the silica nanoparticle suspensions follows the procedures published in the literature. ζ potential of nanoparticles was manipulated by three ways. The first way is to maintain the pH in the silica colloid suspensions constant and vary the dielectric constant of the solvent by adding an amount of alcohol. The second way is
to keep the dielectric constant unchanged while adjust the pH. The third way is to alter both of them. The pH of both the anionic silica suspension and the corresponding cationic binder was varied using H$_2$SO$_4$ or NaOH to maintain the desired pH. Ethanol or IPA was employed to vary the dielectric constant of solvents. A pH value of 5.0 or 7.0 was chosen for the silica suspensions because this value is well away from the region where the hydrolyzed acrylamide groups on the cationic binder ionize and yet far enough above the silica iso-electric point (IEP) to easily maintain suspension stability. The impact of surface charge was next investigated by varying the pH of the cationic polyelectrolyte suspension above and below the iso-electric point, IEP, of the previously adsorbed silica nanoparticles. This approach was preferred over varying the pH of the silica suspensions themselves, since, as will be described in detail shortly, nanoparticles were found to agglomerate at suspension pH values near or below the IEP. Ethanol content in the suspension was varied from 1% by volume to 20% and then finally 50% to vary the dielectric constant. IPA content in the suspension was 50% by volume.

NanoX concentration was kept at 10% by volume in solution (a solids content of 0.5%) to minimize use of raw material. In the case of the EMS silica, the concentration chosen was 5% by volume (a solids content of 2%). The effect of silica concentration was not systematically investigated in the present work but a quantitative impact was only observed with a more than two-fold increase in concentration. Only de-ionized (DI) water was employed for dilution and rinsing in this work.
3.2.2 Graphite Suspensions

Preparation of the graphite platelet suspensions follows the procedures previously published in the literature 43. The pH of the suspensions was maintained at a value of 5 or 7 using H₂SO₄. Again, this value was chosen because it was sufficiently high to ensure suspension stability yet sufficiently low to prevent dissociation of hydrolyzed groups on the cationic binder employed for LBL assembly. Alcohol-free (100% water) or alcohol-containing (50% ethanol or 50% IPA by volume) media were employed for the graphite suspension. The suspensions have a concentration of 5 weight % graphite. The graphite suspensions were ultrasonicated for at least 30 mins before the multilayer assembly, the pH was adjusted after the ultrasonic and just before the assembly formation.

3.2.3 Mixed Nanoparticle Suspensions

Mixed nanoparticle suspensions containing silica nanoparticles and graphite platelets were prepared utilizing the same pH and concentration as the separated nanoparticles suspension. The mixed nanoparticle suspensions were prepared by mixing a certain amount of raw materials into the solvent (including 1% to 50% EtOH or 50% IPA by volume). The suspensions consisted of 5% graphite and 2 % EMS silica, or 5 % graphite and 0.5% NanoX silica. The pH for all the mixed suspensions was adjusted by H₂SO₄ to a value of 5 or 7.
3.2.4 Polymer Solutions

A cationic copolymer consisting of acrylamide and quaternary ammonium salt was purchased from Cytec.Inc. as seen in Figure 3-4. It is used as a “binder” for anionic nanoparticles in the multilayer adsorption. Cationic polyacrylamide adsorption was carried out from aqueous solution with the pH adjusted to the values of 1.0 or 5.0 with H₂SO₄ in de-ionized water. The concentration of the polymer solution at pH of 1.0 is 0.72g/l and at the pH of 5.0 is 0.12g/l. The main reason for a lower concentration at high pH (5.0) is to maintain low viscosity of the solution.

3. 3 Multilayer Formation

3.3.1 Homogeneous Silica Multilayer Formation

A typical LBL self-assembly process for homogeneous silica multilayer formation involving the use of a cationic polyelectrolyte and anionic silica nanoparticles was depicted in Figure 3-7. Homogeneous silica multilayer indicates that the coating only contains polymer and silica. During the process, the substrate is first dipped into the solution of cationic polyacrylamide for 2 min, then rinsed vigorously in the Milli-Q water baths (1 minute total in two baths with vigorous agitation) to remove the un-adhered residue. The sample was then submerged in the anionic silica nanoparticle solution for certain time and rinsed vigorously in other two Milli-Q water baths (1 minute total in two baths with vigorous agitation). This deposition cycle was repeated as many times as desired. The chemical baths remained quiescent during immersion of the samples but were thoroughly agitated between
sample immersions. Polymer immersion time was chosen based on the known rapid adsorption of this material \(^{50,51,154}\). Completion of a single cycle in Figure 3-7 leads to the creation of a “bilayer” composed of a cationic polyelectrolyte layer and an anionic nanoparticle layer.

Figure 3-7 The typical self-assembled multilayer coating process for homogeneous silica multilayer formation. Completion of a single cycle leads to the creation of a “bilayer” composed of a cationic polyelectrolyte layer and an anionic silica nanoparticle layer.

### 3.3.2 Hybrid Multilayer Formation by Competitive LBL (cLBL)

In contrast to homogeneous silica multilayer, **hybrid** multilayer means the coatings contain polymer, silica nanoparticles and graphite nanoparticles.

Competitive LBL (cLBL) assembly from stable mixed heterogeneous nanoparticle suspensions is discussed here firstly for hybrid multilayer preparation. Simultaneous competitive adsorption was studied widely in polymer multilayers \(^{155}\), biochemical \(^{104}\),
Studies of self-assembled monolayer (SAM’s) of mixtures of alkanethiols deposited on gold indicate that the monolayer composition correlates to the suspension composition from which it was made. Whether similar behavior results from mixed nanoparticle suspensions has never been explored. In the present study, we reinvestigated the possibility of creating the nanoparticle hybrid multilayers by this method and demonstrated that coatings comprising two kinds of nanoparticles can be created by the aqueous based LBL technique. In our lab, previous kinetic studies of the two nanoparticles employed in this investigation (silica and graphite) indicate an order of magnitude difference in the adsorption equilibration time. Such a large difference is expected to yield competitive rather than random adsorption and will be explored fully in this investigation. In the investigation, the chemistry for mixed nanoparticle suspensions was varied by different kinds of alcohol addition and salt addition.

The cLBL assembly scheme consisted of initial sample immersion to the cationic polymer solution for 2 minutes for adsorption equilibration followed by thorough rinsing in DI water (two 1 minute increments into first a dirty then clean rinse). The sample was then immersed into the mixed nanoparticle suspension for 10 minutes to ensure equilibration based on previous investigations and then thoroughly rinsed. A single application cycle is named for finish this whole procedure. Additional layers were applied by repeating this cycle without intermediate drying. The final coating was dried by allowing to sitting in ambient overnight prior to characterization. The schematic for cLBL was described in Figure 3-8.
3.3.3 Hybrid Multilayer Formation by Directed LBL (dLBL)

Researches about the directed LBL assembly have already extensively reported in other areas\textsuperscript{158-164}. However, Multilayers containing nanoparticles prepared by directed LBL assembly, to our best knowledge, have never been explored.

Previous LBL investigations have routinely shown that complete coverage of the substrate surface is seldom achieved after the deposition of a single bilayer of two complementary polymers or a polymer binder and nanoparticles\textsuperscript{43, 51, 53, 54, 153, 165}. In most cases, complete substrate coverage is not achieved until after adsorption of at least three to four bilayers. AFM and SEM images have revealed that the initial bilayer adsorbs in the form of islands which grow and coalesce with the deposition of subsequent bilayers\textsuperscript{43, 165}. Submonolayer coverage has been previously observed with
graphite platelets and, under appropriate conditions, silica nanoparticles. The emphasis of previous published investigations has been on depositing a sufficient number of layers so as to achieve a well-defined bilayer thickness. Whereas a transition region at early deposition cycles yielding incomplete substrate coverage has been frequently noted, the implications with respect to multidimensional nanoparticle structure development have yet to be fully exploited.

In our dLBL assembly scheme, the initial, porous layer of deposited graphite platelets is immediately immersed into a suspension of discrete silica nanoparticles, by-passing the application of cationic binder. It is hypothesized that repulsive interactions between the negatively charged heterogeneous nanoparticles will direct the second nanoparticle layer into the interstitial sites which contain exposed cationic binder from the initial layer which attracted the graphite platelets. A layer of discrete heterogeneous domains of nanoparticles will thus be formed from such a directed-assembly scheme. Repetition of this adsorption sequence will create a multilayer architecture composed of a series of heterogeneous two-dimensional arrays. More electrically conductive coatings are expected to achieve by this method because the chances of direct graphite nanoparticle contacts between adjacent arrays is substantially enhanced relative to cLBL or the standard LBL assembly process (to be discussed next). The low contact resistance previously obtained with thick LBL assembled graphite platelet coatings despite the presence of insulating cationic binder makes this approach particularly promising.\(^{43}\)
Figure 3-9 Scheme for dLBL assembly, discrete nanoparticle suspensions were used. The polymer layer between the graphite and silica was eliminated in dLBL assembly.

Figure 3-9 shows the typical dLBL assembly scheme. The dLBL assembly scheme consisted of initial immersion of a sample into the cationic polymer for 2 minutes, followed by a 2 minutes cumulative rinse time in DI water, 10 minutes immersion in graphite suspension, another 2 minutes of cumulative DI water rinsing, immersion into a silica suspension for 2 minutes for adsorption equilibration, and a final 2 minute cumulative DI water rinse. The entire sequence was considered a single application cycle and repeated to form multilayer coatings. Coating was dried as described previously.

3.3.4 Hybrid Multilayer Formation by Standard LBL (sLBL)

In this scheme, the cationic polymer binder necessary for LBL assembly is deposited on the sample surface after application of each discrete nanoparticle layer as in the typical LBL process sequence. In the present study, we
investigate whether such coating non-uniformity will permit sufficient contact between alternating graphite layers to yield highly conducting coatings with high hydrophilicity.

Figure 3-10 Scheme for sLBL assembly. Cationic polymer was applied after each nanoparticle layer

The sLBL assembly scheme was identical to dLBL with the exception that a cationic polymer application step was inserted between the graphite rinse and the silica deposition. This step consisted of 2 minutes immersion into the cationic polymer solution followed by a 2 minute cumulative DI water rinse. Vigorous manual agitation was employed during rinsing of the samples whereas no agitation was employed while the samples were immersed in the polymer solution and nanoparticle suspensions. The scheme for sLBL assembly may be found in Figure 3-10. The sLBL assembly scheme consisted of initial immersion of a sample into the cationic polymer for 2 minutes, followed by a 2 minutes cumulative rinse time in DI water, 10 minutes
immersion in graphite suspension, another 2 minutes of cumulative DI water rinsing, 2 minutes immersion into the cationic polymer solution again followed by a 2 minute cumulative DI water rinse, 2 minutes immersion into a silica suspension for adsorption equilibration, and a final 2 minute cumulative DI water rinse.

3.4. Characterization

\( \zeta \) potential measurements were obtained at room temperature of 25 \(^\circ\)C by dynamic light scattering (Zeta-Plus from Brookhaven Instruments). As will be indicated in the results chapter, \( \kappa a > 10 \) for all suspensions employed in this work and the double layer is thin relative to the particle radius. Consequently, \( \zeta \) potential was calculated using the Smoluchowski approximation \(^{95}\) (to be discussed in results chapter).

Dynamic light scattering was also used to assess nanoparticle diffusivity and, assuming an equivalent hydrodynamic sphere and applying the Stokes-Einstein Equation, the diameter of the nanoparticle. The as-prepared nanoparticle suspensions were found to be sufficiently dilute for stable photon correlation coefficients to be obtained, obviating the need for further dilution.

High resolution SEM images of the deposited surface layers were obtained using a Carl Zeiss NVision 40 Crossbeam® workstation with a LEO Gemini® field emission column. The column is provided with an “in-lens” annular secondary electron (SE) detector. A beam energy of 3kV and WD of \( \sim 3.5\)mm was used. Also, some low magnification SEM images was obtained by using a field emission SEM
An FEI XL-30 System SEM equipped with an Energy Dispersive X-ray Spectrometer (EDS, EDAX Corp.), was employed to monitor changes in the elemental composition of the LBL coatings. Semi-quantitative analysis was performed at a constant accelerating potential of 15 keV, a working distance of 10 mm, an amp time of 51.2 μs and a magnification of 200x. The C, O, and Si K emission intensities were compared to the Au L or Fe L emission intensity for relative analysis with results reported as weight %. A minimum of 3 measurements on each of the two sides of the substrates were taken with the average and standard deviation of all points reported.

AFM images were obtained using a Dimension 3100 (Veeco Metrology Group) operated in constant force mode. Best images were obtained utilizing a tip with a nominal radius of 20 nm (DNP, Veeco) and an image area of 20 x 20 micrometers.

ToF-SIMS (ToF ION IV) was used for static analysis (mass spectra) and dynamic analysis (depth profile and mapping) for the deposited coatings. Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) is a surface-sensitive spectroscopy that uses a pulsed ion beam (Ga) to remove molecules from the very outermost surface of the sample. The dissociated ions (positive or negative, called secondary ions) are removed from atomic monolayer on the surface. These particles are then accelerated into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector (i.e. time-of-flight).

In order to convert the EDS composition data to thickness, we employed
Monte-Carlo electron flight simulations (CASINO Version 2.42, Universite de Sherbrook, Quebec) under the same microscope conditions as those used experimentally. The solid curve in Figure 3-11 depicts the results from such simulations where the k-ratio (the silicon, Si, X-ray intensity, I, from a silica, SiO₂, coating on pure gold relative to that of a pure silicon, Si, substrate, I_ref) is plotted versus the coating thickness for silica component. We note that the plot is linear up to a thickness of at least 1000 nm. Consequently, the following Equation may be used to determine the coating thickness for silica component, \( t \), from an experimental determination of the k-ratio (\( \frac{I}{I_{\text{ref}}} \)):

\[
(t_{\text{SiO}_2}=1508\,nm\frac{I}{I_{\text{ref}}}) \quad \text{Equation 3-3}
\]

Where 1508 nm is the slope of the line in Figure 3-11 and represents the extrapolated coating thickness at which the k-ratio becomes 1. Equation 3-3 is also used to calculate the thickness of pure homogeneous silica multilayers, as will be shown in results chapter (Chapter 4.1).

The simulation for carbon component was reported in our previously investigation. For simplicity, when the thickness attributed to carbon component is below 700 nm, the followed Equation may be applied to obtain the thickness for carbon component.

\[
(t_c=1180.8\,nm\frac{I}{I_{\text{ref}}}) \quad \text{Equation 3-4}
\]

Equation 3-4 is also used to calculate the thickness of pure homogeneous graphite multilayers.
Figure 3-11. Monte Carlo simulations for the Si k ratio \( \frac{I}{I_{\text{ref}}} \) as a function of the thickness of a SiO₂ coating.

The overall coating thickness, \( t \), for hybrid coating may then be obtained utilizing\(^{166}\):

\[
(dt = d_C t_C + d_{\text{SiO}_2} t_{\text{SiO}_2} \quad \text{Equation 3-5})
\]

where \( d \) is the coating thickness density (calculated roughly from EDS weight % data) and \( d_i \) is the density for pure component \( i \) (silica or graphite). Incorporation of adventitious carbon and oxygen on the substrate into the Monte Carlo simulations is found to have negligible impact on the final coating thickness result.

**Dynamic contact angle measurements** were made utilizing a Sigma 701 wetting balance (KSV Instruments). The probe liquid was DI water and the stage was moved at a velocity of 5 mm/min, ensuring quasi equilibrium advancing and receding
contact angles. A minimum of 3 readings were performed per sample. At least 3 back-to-back advancing-receding cycles were performed per sample to ensure that the contact angle did not change with repeated immersions (suggesting loss of material or absorption of water, either of these invalidating the contact angle result). The following expression was used to get the contact angles by the computer program:

\[
(F = L \delta \cos \theta \quad \text{Equation 3-6})
\]

where \( L = 2 \times (\text{width} + \text{thickness}) \), \( \delta \) is the surface tension of liquid (72.8 mN/m for water at room temperature), \( \theta \) is the contact angle. The force, \( F \), is different when the sample was immersed into or pull out from water.

**Electrical contact resistance** was assessed using a custom built hand-press from Carver, as shown in Chapter 2.3. Gold coated platens were attached to swivel points on the press and connected to a power supply. Teflon tape on one platen surface defined a 1 inch x 1 inch contact area into which was placed a 1 in\(^2\) coated sample. The sample was first sandwiched between two conductive compliant sheets of graphite fiber paper (Toray TGP-H-1.0T) to permit the controlled application of a contact pressure of 200 psi for all measurements. The through-plane potential drop at an applied current density of 1 A/cm\(^2\) (6.5 Amps) was read which, when subtracted by the potential drop for the bare substrate and divided by two (the sample being coated on both sides), gave the coating contact resistance, \( R_c \), in units of \( \Omega \cdot \text{cm}^2 \). In other words: \( R_c = RA \). where, R is the through plane resistance of the coating and A is the contact area. The through plane volume electrical resistivity, \( \rho \), of the coating may be obtained from this contact resistance and the estimated thickness, \( t \), of the coating.
using:

\( \rho = \frac{R}{t} \)  \hspace{1cm} \text{Equation 2-10) }

As mentioned in Chapter 2, the coating surface is assuming to conform perfectly to the electrode surfaces. Since this is unlikely in the case of LBL-assembled nanoparticle coatings, Equation 2-11 provides only an upper bound on the volume resistivity in the present study.

**Durability testing** is carried out by immersing the coated substrates into water which was sealed in a glass bottle, then the sealed bottle was put in a 80°C oven for certain period of time (6 days or other time according to different requirement). After the durability test, the samples were dried overnight in ambient environment, and then the properties for the coatings were tested again to compare with the ones prior to test.
Chapter 4 Results and Discussion

4.1 LBL Assembly of Silica Nanoparticles from Ethanol/Water Based Suspensions

As a means for developing a new class of nanostructured materials\textsuperscript{167, 168}, silica nanoparticle electrostatic LBL assembled multilayers on various surfaces has been the subject of interest for many years. LBL silica-gold nanoparticle assembles to control interparticle-distance for construction of plasmatic waveguides was reported\textsuperscript{169}. Organic pigment coated with LBL silica to improve the weatherability and dispersion ability in waterborne systems was another meaningful application\textsuperscript{170}. Hollow sphere\textsuperscript{171} and nanocapsules\textsuperscript{172} could also be obtained by LBL of silica nanoparticles on organic substrate, then followed by the burn out of the organic materials. LBL Silica films were also researched as photoluminescent oxygen sensors\textsuperscript{173}. The effect of temperature on LBL self-assembly of linear polyions and silica multilayers was also investigated\textsuperscript{174}. Silica LBL assembly has been proposed as a means of creating ordered arrays for photonic bandgap applications\textsuperscript{175} and studies of various silica assemblies have appeared\textsuperscript{64}. One interesting application recently investigated is the use of silica to create a textured surface which, after coating with a perfluorinated silane, mimics the super-hydrophobic behavior of lotus leaves\textsuperscript{96, 176-178}. Silica nanoparticle adsorption has also recently been explored as a means of enhancing cellulose fiber retention in papermaking\textsuperscript{170}. The transparency and antireflection properties of such films for their use on windows and car windshields has been
demonstrated. LBL assembly of pure nanoparticle assembly consisting of oppositely charged silica and titania nanoparticles without intervening polyelectrolyte binder layers has also recently been shown to produce superhydrophilic coatings with antifogging properties. The pH dependence of the LBL assembly process for these films as well as films produced using silica and aminopropyl-functionalized silica nanoparticles has been well characterized. One promising application recently was the use of silica LBL assembled thin films, which followed by grafting a polyelectrolyte copolymer to fabricate a thermo-responsive wetting surface. For practical application of the silica coating, the mechanical integrity (durability and adhesion) is extremely important, and the mechanical properties for silica LBL assembled films may be significantly improved by hydrothermal treatment and calcination.

In this sub-chapter, silica nanoparticle LBL assembly on surfaces is evaluated as a means to control the surface hydrophilicity and contact resistance of electrically conducting substrates. Such hydrophilicity arises due to the negative surface charge which results from the dissociation of surface silanol groups on the hydrolyzed silica surface. Hydrophilic surfaces are particularly important in solution flow through capillaries. For example, liquid-water transport through small channels present in otherwise electrically conductive components of proton exchange membrane (PEM) fuel cell can be particularly important for efficient system operation. Capillary-driven instabilities can result in liquid water holdup in channels. In the case of PEM fuel cells, such a holdup may block the channels and prevent reactant
gases going through the channels or to the catalyst sites, which can significant decrease the overall efficiency, as discussed in Chapter 1. Hydrophilic coatings applied to the surfaces of bipolar plate channels in PEM fuel cells have been shown to mitigate this problem\textsuperscript{88}. In the present investigation, silica nanoparticle LBL assembly permits the application of hydrophilic coatings that are sufficiently thin to minimize impact to surface contact resistance of electrically conductive components. Another key advantage of LBL assembly relative to more typical coating methods (e.g., spray, roll, dip) is that low molecular weight species which assist in maintaining silica suspension stability (e.g., alcohols, various ionic compounds) may be rinsed away during processing, leaving behind only the tightly adhered silica nanoparticles on the substrate surface. Consequently, PEM fuel cell system contamination concerns are minimized when liquid flows over a bipolar plate channel coating prepared by utilizing LBL assembly. Furthermore, the thin films prepared by the LBL approach were more stable than the conventional methods\textsuperscript{188,189}.

Polyelectrolyte binder has been demonstrated to have only a small impact on contact resistance in LBL assembled coatings prepared from electrically conductive but relatively hydrophobic nanoparticles (graphite) in our lab\textsuperscript{43}. Consequently, multilayer films produced by LBL assembly of silica nanoparticles using such binder are expected to possess substantially lower contact resistance than the alternate approach which employs oppositely charged silica and titania nanoparticles\textsuperscript{63,69}, while retaining hydrophilic character. Two commercial silica dispersions will be investigated here to examine the detailed kinetics and physico-chemical interactions
responsible for silica multilayer formation. Compared to other reports, a number of aspects of silica LBL assembly are unique to the present investigation:

1) We will systematically evaluate the effect of various suspension parameters, including the dielectric constant, on nanoparticle ζ potential and LBL assembly kinetics with polyelectrolyte. Suspension parameters are chosen based on the Debye-Huckel Equation (Equation 2-1) and thus provide a mechanistic interpretation of LBL assembly behavior. Previous investigations of silica LBL assembly have only examined the effect of suspension pH and ionic strengths on ζ potential and equilibrated all-nanoparticle structures\textsuperscript{182}. The effect of salt addition (ionic strength) on the adsorption of single silica layers onto cellulose fibers using polyelectrolyte has also been evaluated\textsuperscript{179}.

2) Substrates consist of electroplated gold coated onto 316 L stainless steel, one of the main candidate materials for bipolar plates in the PEM fuel cells. Use of charged substrates such as silica is more typical in LBL assembly studies\textsuperscript{47, 63, 69, 96, 179, 181, 182}. In addition, silver electrodes have been used as in LBL assembly studies when silica weight uptake due to multilayer adsorption was monitored by a quartz crystal microbalance (QCM)\textsuperscript{64}. However, to our best knowledge, silica adsorption on gold has not been previously investigated.

3) Volumetric through-plane resistivity will be assessed by the contact resistance measurements. Such evaluations are very necessary in assessing the impact of electrically insulating coatings such as silica multilayer employed in electronics applications and have never been previously performed.
4) Monte-Carlo simulation of the electron scattering and x-ray emission from energy-dispersive spectroscopy (EDS) measurements is used to obtain multilayer thickness. EDS is a more widely accessible research tool than either QCM or spectroscopic ellipsometry.

Both a quantitative assessment of the extent of the electrostatic interaction between nanoparticles in a given suspending medium and subsequent to surface deposition are evaluated by ζ potential measurement.

4.1.1. Silica nanoparticle ζ potential and size

Silica suspensions containing alcohol or free of alcohol were prepared as described in the Experimental section (Chapter 3) with a solids content of 0.5% and 2% by weight for the NanoX and EMS silica, respectively. These suspension concentrations were sufficiently dilute to permit the application of dynamic light scattering for ζ potential and particle size analysis (i.e., stable correlation coefficients may be obtained). Thus, the effect of concentration on ζ potential and particle size was minimized during the LBL assembly.

ζ potential measurements at indicated pH and ethanol content for NanoX and EMS are shown in Figures 4-1-1 and 4-1-2, respectively. The label of “1%” ethanol in these and subsequent Figures for NanoX represents no “added” ethanol in the prepared suspensions. In the case of NanoX, ethanol is present in the raw material (10% by volume) and results in the presence of a small amount of alcohol even in the highly diluted suspension as discussed in Chapter 3. Each point in the Figure
represents the mean value of three measurements. Error bars represents the standard deviation from the average. In general, we note that for both silica types, an increase in the absolute value of the negative $\zeta$ potential results from an increase in the alcohol content in the suspensions. The increase in $\zeta$ potential is consistent with the decrease in suspension dielectric constant as shown in Table 3-1-1 and is consistent with Equation 4-1-1. This is particularly evident at pH values greater than 4, as shown in Figure 4-1-1 and Figure 4-1-2. The isoelectric point (IEP) for both types of silica occurs at a pH value of about 2 and is independent of the alcohol content. Thus, ethanol therefore does not appear to interfere with the extent of silanol dissociation (e.g., through surface adsorption $^{95}$).

Particle size measurement for the silica nanoparticles were performed using dynamic light scattering as a function of pH in regions where the suspension remained stable (pH values above the IEP). Table 4-1-1 shows the results for NanoX silica nanoparticles. The particle size for NanoX is very close to each other all over the pH investigated shown in the table, and the same as EMS silica.

The average particle diameter from all pH values in Table 4-1-1 is 19.0 nm with a standard deviation of 0.3 nm. The measured value is thus close to that expected based on the vendor literature. Polydispersity was found to be quite high in these samples, with an average value of 0.29. The bigger number of the polydispersity value, the broader of the distribution of particle size. At pH values approaching 2, particle sizes substantially greater than this were obtained, indicating agglomeration as the IEP is approached. Suspension stability is a prerequisite for multilayer formation.
Figure 4-1-1. ζ potential of NanoX nanoparticles in 0.5% solids suspension as a function of ethanol content and the pH of the suspending medium.

Figure 4-1-2. ζ potential of EMS nanoparticles in 2% solids suspension as a function of ethanol content and the pH of the suspending medium.
Table 4-1-1. Number average particle diameter and polydispersity versus pH for NanoX suspension

<table>
<thead>
<tr>
<th>pH</th>
<th>size (nm)</th>
<th>standard deviation(nm)</th>
<th>polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.96</td>
<td>18.7</td>
<td>0.6</td>
<td>0.28</td>
</tr>
<tr>
<td>4.07</td>
<td>19.4</td>
<td>0.4</td>
<td>0.29</td>
</tr>
<tr>
<td>5.02</td>
<td>18.7</td>
<td>0.7</td>
<td>0.27</td>
</tr>
<tr>
<td>6.08</td>
<td>19.1</td>
<td>0.6</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table 4-1-2. Number average particle diameter and polydispersity versus pH for EMS suspension

<table>
<thead>
<tr>
<th>pH</th>
<th>size (nm)</th>
<th>standard deviation(nm)</th>
<th>polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.08</td>
<td>66</td>
<td>1</td>
<td>0.11</td>
</tr>
<tr>
<td>4.01</td>
<td>67</td>
<td>2</td>
<td>0.12</td>
</tr>
<tr>
<td>5.07</td>
<td>62</td>
<td>1</td>
<td>0.12</td>
</tr>
<tr>
<td>6.00</td>
<td>66</td>
<td>2</td>
<td>0.14</td>
</tr>
</tbody>
</table>
since large aggregates result in coating non-uniformities. To maximize silica suspension stability, while preventing hydrolysis of the pre-adsorbed cationic polyacrylamide, the pH of the silica suspensions maintained at a value of 5.0 for all investigations of multilayer formation in this section.

Results about particle size and polydispersity for the EMS nanoparticles are shown in Table 4-1-2. The average particle diameter is 65.2 nm with a standard deviation of 2.2 nm. Once again, the measured particle size was close to the vendor-advertised value. At pH values approaching 2, particle size was found to increase, again indicating agglomeration of silica nanoparticles as the IEP is approached. The average polydispersity was found to be rather high at 0.12. Thus, the EMS silica nanoparticles has a narrower distribution compared to NanoX silica particles.

4.1.2. Multilayer formation with the Cationic Polymer at pH 1 (below the IEP of silica nanoparticles)

For both commercial silica nanoparticles investigated, the adsorption reaches equilibrium very rapidly. The impact of immersion time in NanoX silica suspension containing 0.5(wt) % solids and 50(V)% ethanol with a pH value of 5 is shown by the EDS data in Figures 4-1-3 and corresponding thickness in Figure 4-1-4. The polymer has a concentration of 0.72 g/l at pH 1.0. Consequently, the ζ potential of the NanoX silica nanoparticles was -38 mV in the silica suspension and 5.0 mV in the polymer suspension. Figure 4-1-3 depicts the weight % Si as a function of the number of
biayers deposited. Error bars in this Figure represent +/- one standard deviation from the average of a total of 3 measurements on each of two sides of the sample. Figure 4-1-4 depicts the corresponding thickness data obtained by applying Equation 3-3 to experimental \( k \) ratio data. Only the average thickness is depicted in this Figure. In spite of negligible electrostatic attraction between the cationic polymer and the previously deposited silica nanoparticles while in the polymer solution (i.e. silica owns positive surface charge and polymer is also positive charged), we note from Figures 4-1-3 and 4-1-4 that substantial Si uptake occurs. No Silica deposition is observed if the cationic polymer is not applied, and the small amount of Si detected by EDS on the bare substrate (~0.5% by weight) results from the underlying stainless steel formulation. There must be some other attraction interaction other than electrostatic association between the polymer and silica particles. One possible source of attraction is hydrogen bonding between the acrylamide groups on the polymer (as seen in Figure 3-3) and the weakly acidic silanol groups (as shown in Figure 3-1). In the previously investigation\(^{51}\), cationic polyacrylamide binding to basic functional groups through non-electrostatic association has been clearly demonstrated. Figures 4-1-3 and 4-1-4 show that there is only very little difference in terms of silica loading as a function of time for 1 and 2 minute immersions, indicating rapid equilibration of surface coverage within 1 minute. A substantial drop in nanoparticle deposition amount is observed at an immersion time of 10 seconds. Uptake is found to be linear with the number bilayers deposited within the number of bilayers investigated, regardless of immersion time. From a linear fit after surface coverage
equilibration (2 min.), the bilayer thickness obtained is found to be 15.6 nm with a correlation coefficient of 0.98. This value is close to the nanoparticle diameter obtained using dynamic light scattering (Table 4-1-1, 19.0 nm) and suggests that the substrate surface is almost completely covered by silica nanoparticles after the

Figure 4-1-3. Si uptake (as measured via EDS) as a function of the number of bilayers deposited from 10% by volume NanoX suspension at pH 5 and 50% ethanol by volume in water. Immersion time as indicated. Cationic polymer has a concentration of 0.72 g/l at pH 1. Dashed line is for 2 min.
Figure 4-1-4. Coating thickness corresponding to Figure 4-1-3

Figure 4-1-5 SEM image at 100k magnification of 8 bilayers of NanoX silica nanoparticles deposited onto electroplated gold via LBL assembly prepared from suspension having 50% ethanol
application of only a single bilayer. The picture in Figure 4-1-5 shows a high resolution SEM image of the coating, which consists of 8 bilayers of NanoX silica nanoparticles deposited by LBL assembly with cationic polyacrylamide. It may be seen that the deposited nanoparticles were very compact, and the gold substrate is completely covered by silica nanoparticles.

To evaluate the impact of nanoparticle ζ potential while in suspension on silica adsorption during LBL assembly, the alcohol content of the suspension was decreased from 50% ethanol by volume to 20% and finally 1% (no added alcohol). According to the results shown in Figure 4-1-3, immersion time in the silica suspension was maintained at 2 minutes to ensure adsorption equilibrium. Loading results with respect to wt. % Si as a function of bilayer numbers are shown in Figure 4-1-6 and the associated thickness data for the coating obtained using Equation 3-3 are shown in Figure 4-1-7. We note that reduction in particle ζ potential through decreasing alcohol content yields a substantial reduction in loading, with an equilibrated average bilayer thickness of 5.4 nm in the case of 1% suspension (one third of that obtained with 50% ethanol). Electrostatic interaction between the charged nanoparticles in the silica suspension at pH 5 and the pre-deposited cationic polymer is thus also a crucial important component in multilayer formation in addition to immersion time. Changes to multilayer thickness due to alternation of nanoparticle suspension conditions may be predicted qualitatively on the basis of ζ potential measurement. This result is consistent with the previous investigations of silica LBL assembly using titania\textsuperscript{181}. 
Figure 4-1-6. Si uptake (as measured via EDS) as a function of the number of bilayers deposited from 10% by volume NanoX suspension at pH 5 and % ethanol by volume in water as indicated on plots. Immersion time is 2 minutes in every case. Cationic polymer has a concentration of 0.72 g/l and a pH value of 1.0.

Figure 4-1-7. Coating thickness corresponding to Figure 4-1-6.
Figure 4-1-8. Si uptake (as measured via EDS) as a function of the number of bilayers deposited from 5% by volume EMS suspension at pH 5 and 50% ethanol by volume in water. Immersion time as indicated. Cationic polymer has a concentration of 0.72 g/l and a pH value of 1.0. Dashed line is for 2 min.

Figure 4-1-9. Coating thickness corresponding to Figure 4-1-8.
Figure 4-1-10. Si uptake (as measured via EDS) as a function of the number of bilayers deposited from 5% by volume EMS suspension at pH 5 and % ethanol in water by volume as indicated on plot. Immersion time is 2 minutes in every case. Cationic polymer has a concentration of 0.72 g/l and a pH value of 1.0.

Figure 4-1-11. Coating thickness corresponding to Figure 4-1-10. Dashed line is for 50% ethanol by volume.
The corresponding results with EMS silica are shown in Figures 4-1-8 through 4-1-11. The ζ potential of the EMS nanoparticles in the pH 5 silica suspension is -37.5 mV and in the pH 1 polymer solution is 5.9 mV. Thus, as in the case of NanoX, when the pre-deposited silica multilayer is immersed in polymer solution, little electrostatic attraction is expected between the polymer and the nanoparticle surface. Adsorption equilibration time is found to be comparable for both types of silica (~1min), as seen in Figure 4-1-8 and 4-1-9. The primary difference with respect to NanoX is the substantially greater Si uptake and coating thickness which may be attributed to the larger size of the EMS nanoparticles. In addition, in Figure 4-1-9 we note that the dependence of thickness on the number of bilayers deposited is no longer linear but has a logarithmic appearance even at the immersion time required for equilibration of surface coverage (i.e. the bilayer thickness begins at a value below that of the diameter of a single nanoparticle and decreases with each more bilayer). Such behavior may arise from the enhanced cumulative repulsion between the successive applications of EMS nanoparticles and the associated substrate surface (although the ζ potential of individual NanoX and EMS nanoparticle is comparable).

Bilayer thickness equilibration occurs after 4 bilayers have been deposited. As with NanoX, the thickest bilayer is obtained with 50% ethanol and with 2 minutes immersion and, after 4 bilayers have been deposited, has a value of 42.2 nm. This value is substantially lower than the EMS nanoparticle thickness expected (Table 4-1-2, 65.2 nm) and suggests that the equilibrated EMS bilayer is more porous (65%
4.1.3 Multilayer formation with the cationic polymer at pH 5 (above the IEP of the silica nanoparticle)

The impact of increasing the absolute value of the (negative) surface charge of previously deposited silica nanoparticles while in polymer solution was next investigated. The kinetic studies discussed in the previous section were repeated with the only change being an increase in the pH of the polymer solution from 1.0 to 5.0. This value is well above the IEP of both types of nanoparticles and results in a ζ potential of -23.7 mV for NanoX and -27.3 mV for EMS while in the polymer solution (polymer solution has no alcohol, so the 0% curves should be used when Figure 4-1-2 is applied). Under this situation, the electrostatic attraction between pre-deposited silica nanoparticle and ongoing adsorbing polymer would be expected to increase since silica is negatively charged in polymer solution at pH 5 and polymer is positive charged. Results for both NanoX and EMS nanoparticles about Si uptake and thickness as a function of the bilayer numbers are shown in Figures 4-1-12 through 4-1-15. The compositions for nanoparticle suspensions and polymer solutions are also shown in Figure 4-1-12 and Figure 4-1-14. The most surprising change in behavior relative to the pH 1 polymer solution is that Si uptake and corresponding thickness are substantially reduced instead of expected increase. Maximum equilibrated bilayer thickness is 7.4 nm for NanoX and 22.3 nm for EMS. These
values represent a reduction in loading of 50% relative to the pH 1 polymer solution data. This change in uptake with \( \zeta \) potential is opposite that previously described with alcohol content and is counter-intuitive.

**Figure 4-1-12.** Si uptake (as measured via EDS) as a function of the number of bilayers deposited from 10% by volume NanoX suspension at pH 5 and 50% ethanol in water by volume. Immersion time as indicated. Cationic polymer has a concentration of 0.13 g/l and a pH value of 5. Dashed line is for 2 min.
Figure 4-1-13. Coating thickness corresponding to Figure 4-1-12.

Figure 4-1-14. Si uptake (as measured via EDS) as a function of the number of bilayers deposited from 5% by volume EMS suspension at pH 5 and 50% ethanol in water by volume. Immersion time as indicated. Cationic polymer has a concentration of 0.13 g/l and a pH value of 5. Dashed line is for 2 min.
Such behavior is not consistent with the standard Sjutjens-Fleer description of polymer adsorption in that an decrease of ionic strength, $\kappa$ (due to less ions in polymer solution at pH 5 versus pH 1), and the associated increase in the substrate and adsorbate (negative) $\zeta$ potentials is expected to enhance polymer adsorption. Analogous behavior has been observed in a previous study of the effect of ionic strength on cationic polyacrylamide adsorption onto a previously deposited silica nanoparticle surface. Previous investigation of similar cationic polyacrylamide adsorption on charged and uncharged surfaces also encountered such behavior. A model has been developed to account for such behavior which recognizes that adsorption energy is attenuated by the presence of solvation energy (i.e., the attraction of water molecules for both substrate and adsorbate). Thus, as substrate-adsorbate
attraction increases, so does attraction to the solvent and a point is reached where an adsorption maximum is reached, whereupon uptake paradoxically declines with increasing interaction energy. Figure 4-1-16 shows the scheme for this model. Such a model is consistent with the observations in the present investigation associated with increasing polymer pH and the absolute value of the (negative) ζ potential.

Interestingly, a maximum in silica deposition with increasing ζ potential was observed for silica nanoparticle LBL assembly with oppositely charged aminopropyl-functionalized silica nanoparticles in the recently study182. One possible explanation provided in that investigation was that increased silica nanoparticle ζ potential enhanced electrostatic repulsion between intervening layers and between nanoparticles in the same layer, and thus reduced nanoparticle deposition, presumably while the aminopropyl-functionalized silica particles remained at a fixed bilayer thickness. Separation of the contribution to the coating thickness by each of the two oppositely charged nanoparticles would have strengthened this hypothesis. In addition, one must account for the contrasting behavior observed when titania is used181. Regardless, the applicability of ζ potential correlations to adsorption behavior in all-nanoparticle versus nanoparticle-polyelectrolyte LBL systems is uncertain and more research in the field (both experimental and theoretical) is required.
Figure 4-1-16. The relationship of silica adsorption amount and the electrostatic attraction force between silica particles and polymer. The symbol “+” represents the positive charge on the polymer and the dash “-” represents the negatively charged, pre-adsorbed silica particles. Maximum silica adsorption is reached (point B) where polymer/particle electrostatic attraction and solvation energy are optimized. Less silica adsorption occurs when the electrostatic attraction force is too weak (point A) or solvation energy is too strong (point B).

4.1.4 Silica multilayer surface energetics

The impact of silica suspension alcohol content on the advancing contact angle of the NanoX and EMS coatings is depicted by Figures 4-1-17 and 4-1-18 for equilibrated multilayers (2 minutes immersion in silica suspension). For NanoX, the
coated surface is more hydrophilic when the average thickness of the coating increases by increasing alcohol content. The most hydrophilic surface in Figure 4-1-17 has a contact angle of 17° after 8 bilayers from 50% ethanol suspension and pH 1 polymer solution versus a contact angle of 84° for the bare substrate. Substantial contact angle hysteresis was observed, with the receding contact angle being lower than the advancing contact angle in every case. The reduction in advancing contact angle observed with increasing silica uptake may be explained by alteration of substrate surface coverage as described by the Johnson-Dettre model for contact angle hysteresis\textsuperscript{126}.

![Graph showing contact angle vs. dips for different ethanol concentrations and pH values](image)

**Figure 4-1-17.** Advancing contact angle of NanoX coatings. The numbers in the Figure indicates the % by volume ethanol in silica suspension and the pH of the cationic polymer solution.
Interestingly, despite the substantially lower uptake, the wetting behavior of the NanoX coating prepared from pH 5 polymer solution is nearly the same as that prepared from pH 1 polymer solution (50% ethanol in the silica suspension for both cases) and among the most hydrophilic of all samples. According to the Johnson and Dettre model, such wetting behavior indicates comparable silica surface area coverage for the two sets of samples (50%, pH1 and 50%, pH5). If this is the case, then the pH of the polymer solution is not only impacting the porosity of each bilayer, but also the extent of bilayer interpenetration during LBL assembly. This is not unreasonable in light of the fact the extent of polymer adsorption onto previously deposited nanoparticles will be mediated by a change in polymer solution pH and associated nanoparticle $\zeta$ potential.
The surface wetting behavior is somewhat different in the case of EMS (Figure 4-1-18) in that the advancing contact angle of the coatings appears to be relatively insensitive to changes in alcohol content of the silica suspension from which they were obtained. Such behavior is consistent with a high degree of bilayer interpenetration. As in the case of NanoX, wetting hysteresis was observed. The most hydrophilic surface was observed in the case of EMS coatings is 10° after 8 bilayers from 50% ethanol suspension.

Furthermore, the wicking test on the actually fuel cell serpentine gas-flow channels was performed in order to better evaluate the wettability of the coated bipolar plates, as shown in Figure 4-1-19. The plate was coated by 8 bilayers of NanoX Silica multilayer, deposited from 50(V)% ethanol suspension, and cationic polymer with a concentration of 0.72 g/l and a pH value of 1.0. During the test, one drop of water with the volume of about 0.02ml was dropped in the channels. Figure 4-1-19a showed that the water drop on the bare gold bipolar plate was not expanded, indicating the substrate was very hydrophobic, consistent with the contact angle results. Figure 4-1-19b showed the wicking results on the coated bipolar plate, and the water expanded to about 1.6 inch in length. It was also worth mention that the water droplet wet the coated plate nearly instantaneously (<1s). The wicking test showed that the coating was very hydrophilic and it may be expected to remove the water produced in the fuel cell enough quickly to avoid water holdup.
Figure 4-1-19 Wicking results on (a) bare gold bipolar plate; (b) coated bipolar plate, the plate was coated with 8 bilayers of NanoX silica deposited from 50% ethanol NanoX suspension. Cationic polymer has a concentration of 0.72 g/l and a pH value of 1.0.

4.1.5 Silica multilayer contact resistance

Figure 4-1-20 plots contact resistance values for equilibrated (2 minutes immersion in silica suspension) NanoX coatings. The contact resistance monotonically increases with the number of bilayers deposited and qualitatively corresponds to Si uptake. A more quantitative comparison is reached by dividing the data in Figure 4-1-20 by corresponding coating thickness (Figures 4-1-4 according to Equation 2-11) to obtain volumetric through-plane resistivity. The results are shown in Figure 4-1-21. We note that only in the case of the pH 5 polymer solution does the
volumetric resistivity appear to plateau to a characteristic value of 1.63 kΩ-cm. This value is within the range required for electrostatic discharge of electronic components. This value is also about half of that obtained from a comparably thick coating deposited from a polymer solution at pH 1 and a silica suspension containing 1% ethanol (3.17 kΩ-cm at 8 bilayers, compare Figure 4-1-7 and Figure 4-1-13), which has the same average thickness. However, the same average thickness between the two coatings is associated with enhanced hydrophilicity (higher silica surface coverage) in the case of the coating prepared from a pH 5 polymer solution. This observation suggests that the coating prepared from the pH 5 polymer is more densely packed and actually thinner, perhaps yielding greater opportunity for direct electrical contact between the two conducting plates. However, analysis of all coatings subsequent to contact resistance testing did not reveal any damage within the resolution of our SEM instrumentation. The characteristic volumetric electrical resistivity of all coatings is substantially less than the electrical resistivity of fused silica (~10^{15} kΩ-cm).

The volumetric resistivity for the other coatings is just observed to begin to plateau in Figure 4-1-21. Such behavior suggests that a uniform coating structure has not been achieved after the application of 8 bilayers. The maximum resistivity observed for coatings prepared from pH 1 polymer solution is 5.85 kΩ-cm.

Contact resistance data for EMS nanoparticle coatings is shown in Figure 4-1-22 and the corresponding volumetric resistivities are shown in Figure 4-1-23. Whereas the contact resistance values are an order of magnitude higher than NanoX coatings with
a similar number of bilayers, volumetric resistivities scale to roughly twice than that of the NanoX coatings. Unlike the NanoX coatings, EMS coatings prepared from pH 1 polymer solution exhibit characteristic volumetric resistivities ranging from 12.4 to 18.2 kΩ-cm. Coatings prepared with EMS silica are thus insulating materials. As with the NanoX coatings, EMS coatings deposited with a polymer solution at pH 5 has a contact resistance and volumetric resistivity substantially less than coatings with similar thickness prepared from pH 1 polymer solution, suggesting a higher nanoparticle packing density for coatings prepared from a pH 5 polymer.

![Contact Resistance Graph](image)

**Figure 4-1-20** Contact resistance, $R_c$, of NanoX coatings. The key in the Figure indicates the % by volume ethanol in silica suspension and the pH of the cationic polymer solution.
Figure 4-1-21. Volumetric electrical through plane resistivity associated with Figure 4-1-20.

Figure 4-1-22. Contact resistance, $R_c$, of EMS coatings. The key in the Figure indicates the % by volume ethanol in silica suspension and the pH of the cationic polymer solution.
Figure 4-1-23. Volumetric electrical resistivity corresponding to Figure 4-1-23.

4.1.6 Conclusions

A silica nanoparticle LBL assembly was investigated as a unique method of controlling the surface wetting properties while maintaining a low electrical surface contact resistance of metallic substrates employed as bipolar plates in PEM fuel cells. Nanoparticle adsorption was found to occur rapidly, with adsorption equilibrium obtained after only 1 minute and coating thickness which is nearly linear with respect to the number of bilayers deposited.

Silica nanoparticle $\zeta$ potential was systematically examined by altering both the pH and alcohol (ethanol) content of the suspensions. Over the studied pH range, silica $\zeta$ potential was from -56.8 mV (pH 5) to 5.0 mV (pH1). The dependence of adsorption
amount, thickness, wettability, and contact resistance of the final LBL-assembled coatings on the silica nanoparticle $\zeta$ potential is presented.

An increase in the absolute value of the (negative) $\zeta$ potential in NanoX silica suspension by ethanol addition was found to increase the bilayer thickness to an average value as high as 82% of the individual nanoparticle diameter, suggesting that nearly complete surface coverage may be achieved after the application of only a single nanoparticle-polymer bilayer (a coating thickness as 15.6 nm). A more porous bilayer structure was observed with larger silica EMS nanoparticles with a maximum bilayer thickness of 42.2 nm or 65% of the nanoparticle diameter.

Counterintuitively, less silica adsorption was observed if the $\zeta$ potential of previously deposited silica nanoparticle was changed from 5.0 mV to -23.7 mV while immersed in the cationic copolymer suspension. The implication of such behavior was that copolymer adsorption is inhibited by substrate-solvent interaction.

Wetting measurements demonstrate that silica LBL assembly results in a substantial reduction in contact angle from 84° on the bare substrate surface to as low as 15° after the application of a single bilayer and 10° after the application of 8 bilayers.

Monotonic increase in coating contact resistance is observed with an increase in the thickness with a characteristic volumetric resistivity as low as 1.63 k$\Omega$-cm with NanoX silica. This value is within that required for numerous conductive coating applications and is substantially less than fused silica. Coatings prepared from LBL assembly of EMS silica nanoparticles have been characterized as electrical insulators.
4.2 LBL Assembly of Multi-Dimensional hybrid Graphite/Silica (NanoX) Nanoparticle Arrays on Gold

LBL (LBL) assembly consisting of 5 – 10 nm thick graphite platelets and 20 nm diameter silica spheres is investigated as a method for the fabrication of multi-dimensional composite arrays to be employed as electronic component coatings. LBL assembly of graphite platelets has recently been demonstrated to yield low electrical contact resistance coatings on metallic bipolar plate surfaces for potential electrochemical applications such as proton exchange membrane (PEM) fuel cells\(^{43}\). LBL assembly of silica nanoparticles has also been found capable to control their surface water wetting properties on identical substrates but at the expense of increased electrical contact resistance. For example, a 100 nm thick coating of silica nanoparticles LBL assembly has a contact resistance of 41 m\(\Omega\)-cm\(^2\). For a state-of-the-art proton exchange membrane (PEM) fuel cell operating at a load of 1 A/cm\(^2\), this value of contact resistance means about 7 % power loss\(^{192}\). While thinner coatings possess lower contact resistance, they have been found to be less durable. In the present study, we wish to investigate whether heterogeneous nanoparticles may be incorporated into a composite hybrid coating which could possess the hydrophilic properties of silica nanoparticles while retaining the high electrical conductivity of graphite platelets. There are many advantages of LBL assembly compared to other methods, such as low cost, conformal coating, and nanoscale thickness control\(^{55}\). Consequently, three various LBL assembly schemes (cLBL, dLBL and sLBL, as described in Chapter 3) are explored to obtain a detailed understanding of multilayer
formation and functional performance.

To form heterogeneous nanoparticle arrays on surface via LBL assembly, previous attempts have typically focused on adsorption onto previously defined micron-scale features, such as microcontact printing (i.e., “stamping”)\textsuperscript{55} and micromachining\textsuperscript{193}. An alternate approach for nanostructured arrays involves the assembly of colloidal particles under capillary forces \textsuperscript{56} as well as the self-arrangement of nanocrystals into superlattices \textsuperscript{56}. The space between the nanoparticles may then be filled utilizing various techniques such as vapor phase deposition. However, as is the case with nanolithography techniques \textsuperscript{194}, such approaches are much more difficult to implement in practice than if a method which relies entirely LBL assembly can be developed. Designing such a method is the key objective of the present investigation.

Fundamental aspects of this investigation include: (a) the role of competitive nanoparticle adsorption on LBL-assembled coating composition, (b) the use of electrostatic nanoparticle-nanoparticle and nanoparticle-surface interactions for the directed LBL assembly of heterogeneous multi-dimensional arrays, (c) the impact of the resultant coating structure and thickness on electrical contact resistance, and (d) the impact of surface heterogeneous domain chemistry and morphology on wetting.

4.2.1 cLBL

Composite coatings assembled by cLBL were prepared from stable mixed suspension of graphite platelets and silica nanoparticles as described in the previous Experimental
Figure 4-2-1 depicts the variation of total coating thickness with the number of deposition “cycles” in comparison to pure silica and pure graphite LBL coatings, where each cycle consists of application of the cationic polymer followed by immersion into the mixed suspension, with thorough rinsing in-between (i.e., each cycle represents a bilayer of polymer and graphite/silica composite). A minimum of three random measurements of each sample are evaluated to obtain the average and standard deviation of thickness. Four different ethanol contents were investigated since pure silica nanoparticle adsorption was previously found to be significantly influenced by the dielectric constant of the solvent. The “%” label in the Figure 4-2-1 means the volume % ethanol. Also, depicted in the Figure are the previous results obtained with pure graphite (in water, labeled “Gr” in the Figure) and pure silica (in 50% ethanol, labeled “Si” in the Figure). Immersion time in the nanoparticle suspensions is 10 minutes in every case to ensure equilibration of adsorption. As previously mentioned, the polymer layer contributes negligibly to the thicknesses reported in Fig. 4-2-1 because the presence of nitrogen (an element unique to the polymer) cannot be detected in the EDS spectra.

The thickness for all samples shown in Fig. 4-2-1 increases linearly for the initial four deposition cycles. The solid and dashed lines in Fig. 4-2-1 indicate linear fits through the pure graphite and silica coatings, respectively. The bilayer thicknesses for the composite coatings fall between that of pure silica (16 nm) and that of pure graphite (51 nm). The bilayer thickness of the pure silica is consistent with almost complete surface coverage of silica nanoparticles. That for the graphite (well in excess
of the thickness of a single platelet) has been previously demonstrated to result from clustering and tilted orientations of the graphite platelets on the gold substrate surface.

![Graph showing coating thickness vs cycle number for different materials and concentrations.](image)

**Figure 4-2-1.** Overall coating thickness obtained from cLBL assembly scheme in comparison to pure silica (“Si”) and pure graphite (“Gr”) coatings. Cationic polymer has a concentration of 0.72g/l with a pH value of 1.0. Immersion time in polymer solution is 2 minutes and in mixed nanoparticle suspension is 10 minutes.

Similar platelet clustering and tilted orientations are also observed in SEM images of the cLBL assembled coatings, as are shown by the SEM images in Figure 4-2-2. The cLBL assembled coatings shown in Figure 4-2-2 are prepared from mixed suspension in 50 volume % ethanol. Comparison of Fig. 4-2-2 (a) obtained for the bare substrate surface to that of Fig. 4-2-2 (b) obtained after one cycle indicates that
distinct domain separation between the graphite and silica nanoparticles occurs during cLBL assembly. In other words, no silica nanoparticles are found to be absorbed onto graphite platelet surface, while the portion of the substrate onto which graphite platelets have not adsorbed is coated with silica nanoparticle. The electrostatic repulsion force between the heterogeneous nanoparticles resulting from the high negative ζ potential observed for both graphite and silica at the pH of the suspending medium are responsible for this morphology. The distinct domain separation persists within the cycles investigated.

The composition of coatings prepared from the mixed suspension is described by Figure 4-2-3, where the ratio of weight % carbon / weight % silicon (C/Si) obtained from EDS measurement is plotted versus the number of deposition cycles. Data for the sLBL and dLBL assembled coatings in this figure will be discussed in the next section. The cLBL assembled coating data is clearly labeled with the volume % ethanol. C/Si ranges from a high value of 10.1 for a single bilayer deposited from 1% ethanol to a low value of about 2.1 for four bilayers. These values are all substantially lower than the value of 21.4 in the mixed suspension (indicated by the dashed line in Fig. 4-2-3) and suggest that competitive adsorption favors the silica nanoparticles due to differing adsorption kinetics. Previous studies shows shows that silica adsorption reaches equilibrium very rapidly within 1 minute and graphite adsorption takes 10 minutes to reach equilibrium. This conclusion is supported by the fact that the graphite nanoparticles deposited in the initial layer from the mixed
Figure 4-2-2. SEM images at 20-25kX of the surface of (a) bare substrate and cLBL assembled coatings after (b) 1 Cycle, (c) 2 Cycles, and (d) 3 Cycles. The mixed suspensions contain 50% ethanol by volume in water with a pH value of 5.0. The white cycle is used to identify the exposed graphite platelet surface free of silica nanoparticles and illustrate the morphological differences relative to the graphite platelet which have been deposited during the previous cycle and covered by silica nanoparticles.
Figure 4-2-3. Carbon to silicon weight % ratio from EDS measurements for various LBL assembled coatings. The % indicates the volume % ethanol in mixed nanoparticle suspension (competitive LBL assembly). Notations dLBL and sLBL are defined in the text. The dashed line in the Figure represents the composition of the mixed nanoparticle suspensions.

We note from Fig. 4-2-3 that C/Si rapidly declines with the application of additional bilayers until a plateau is reached at about 3 bilayers. This result coincides
with increased platelet coverage of the substrate surface observed in Figure. 4-2-2 (b) through (d) and suggests that the graphite platelets are more readily adsorbed onto the bare substrate. Our previous investigation also gets this conclusion\textsuperscript{43}. A white circle is used in Fig. 4-2-2 (d) to identify an exposed graphite platelet surface and illustrate the morphological differences relative to graphite platelets which have been deposited during previous immersion cycles and covered by silica nanoparticles.

The advancing contact angle of water for coatings with three cycles prepared from mixed suspensions of varying alcohol content is described in Table 4-2-1, in comparison to the results obtained from pure graphite with 8 bilayers and pure silica with 8 bilayers as well as that of the bare gold substrate. The average of 3 measurements is reported in the table with a standard deviation of 2° in every case except bare substrate, for which the value is 5°. The receding contact angle was found to be 18° with standard deviation of 5° in every case. The results are thus consistent with Johnson and Dettre\textsuperscript{126, 195} model, i.e. a surface composed of heterogeneous domain areas larger than molecular scale has advancing and receding contact angles are indicative of the most hydrophobic and the most hydrophilic domains, respectively. Such insensitivity is evident in Table 4-2-1 in that the advancing contact angle of all cLBL composite coatings is more close to that of the pure graphite than pure silica, despite the sparse nature of the exposed graphite platelet domains observed in Fig. 4-2-2 (d).

On the other hand, the Johnson and Dettre model also predicts that as domain size decreases, sensitivity to surface chemical composition increases until the behavior
approaches that of the Cassie Equation \(^{134}\) at molecular scales. Thus, control over domain size will permit control over surface wetting while, at constant total surface area of electrically conducting domains, maintaining good contact resistance. We will examine whether such control is feasible in the subsequent adsorption schemes to be investigated in this study.

**Table 4-2-1. Advancing water contact angle on the surface of cLBL assembled coatings prepared from three cycles in mixed nanoparticle suspensions of varying volume % ethanol as indicated.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si(^1)</th>
<th>Gr(^1)</th>
<th>1%</th>
<th>10%</th>
<th>30%</th>
<th>50%</th>
<th>Bare Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advancing Contact Angle ((^{\circ}))(^H)</td>
<td>20</td>
<td>47</td>
<td>36</td>
<td>39</td>
<td>38</td>
<td>40</td>
<td>84</td>
</tr>
</tbody>
</table>

\(^{H}\) Standard deviation is 2\(^{\circ}\) in every case except bare substrate, for which value is 5\(^{\circ}\).

Receding contact angle is 18\(^{\circ}\) with standard deviation 5\(^{\circ}\) in every case.

\(^1\) Data for 8 bilayers of pure silica and graphite nanoparticle coatings are labeled as “Si” and “Gr” respectively.

In addition to surface chemistry, surface morphology is known to influence wetting behavior. For example, according to the well known Wenzel Equation (\(\cos \theta = r \cos \theta_t\)), the observed contact angle should decrease with increasing roughness if the true contact angle is less than 90\(^{\circ}\)\(^{131}\). The surface morphology of some coatings prepared utilizing cLBL was investigated via AFM. The root mean square (rms) roughness data
obtained from 20 m x 20 μm surface areas of a coating prepared from a mixed suspension containing 50% ethanol (labeled as “50%”) are shown in Figure 4-2-4. The corresponding results for 8 bilayer coatings prepared from pure graphite suspensions and pure silica suspensions are also shown in the Figure by the solid and dashed lines, respectively. We note that the surface roughness of the cLBL assembled coatings is intermediate between the two pure coatings and that a plateau is attained after the application of about 3 bilayers (as indicated by the solid line obtained from a

![Figure 4-2-4. AFM rms roughness obtained from 20×20µm areas of cLBL assembled coatings prepared from mixed suspension containing 50% ethanol. Data for 8 bilayer coatings prepared from pure graphite suspensions (in water) and pure silica suspensions (in 50% ethanol) with pH 1 polymer are also shown in the Figure by the solid and dashed line, respectively.](image)

Figure 4-2-4. AFM rms roughness obtained from 20×20µm areas of cLBL assembled coatings prepared from mixed suspension containing 50% ethanol. Data for 8 bilayer coatings prepared from pure graphite suspensions (in water) and pure silica suspensions (in 50% ethanol) with pH 1 polymer are also shown in the Figure by the solid and dashed line, respectively.
second order fit to the data in Fig. 4-2-4). This number of bilayers is comparable to that where the coating composition equilibrates (Fig. 4-2-3, the C/Si ratio remains constant after 3 bilayers) and the substrate surface in nearly completely covered by graphite platelets. Table 4-2-2 shows the advancing contact angle on cLBL assembly surface prepared from suspensions having 1% ethanol with different cycles. We note from Table 4-2-2 that an increase in the roughness of the composite surface does not account for the observed advancing contact angle increase relative to silica. Thus, surface chemical composition dominates the wetting behavior rather than surface morphology in the case of cLBL assembly of the heterogeneous nanoparticles used in our investigation.

A key objective in this investigation is control over coating electrical properties. Figure 4-2-5 is a plot of coating contact resistance versus thickness for coatings prepared from mixed suspensions of varying alcohol content. Also included in the Figure are pure graphite and silica data from coatings prepared utilizing various process conditions. The pure silica and graphite are fit by solid and dashed lines, respectively. In the case of coatings prepared from a given alcohol content as well as
Figure 4-2-5. Contact resistance as a function of thickness for pure Si and Gr (solid and dashed lines, respectively) as compared to cLBL assembled coatings from mixed nanoparticle suspensions containing varying volume % ethanol as indicated

The pure silica and pure graphite coatings, contact resistance increases monotonically with thickness. In general, coatings prepared from mixed suspensions have contact resistances which fall between those of pure silica and pure graphite coatings. Contact resistances at the higher thicknesses are closer to those of pure silica than pure graphite.

Thus, a reduction in contact resistance over pure silica may be obtained at a given coating thickness utilizing cLBL assembly (figure 4-2-5), but at a substantial loss in surface hydrophilicity (Table 4-2-1).
All of the coatings discussed in this section were prepared with the cationic polymer suspension at a pH value of 1 with a concentration of 0.72g/l. The pH value of the cationic binder suspension has previously shown to have a significant impact on the absolute amount of adsorbed amount of silica nanoparticles as well as the kinetics of graphite platelet adsorption from pure suspensions\textsuperscript{43}. In the present investigation, we have found that a pH value of 5 and a lower concentration of 0.13g/l for the cationic polymer solution did not appreciably alter coating composition or performance in the case of the mixed nanoparticle suspensions. For example, when a pH 5 polymer solution is employed, a 4 cycles coating obtained from a mixed suspension having 50% ethanol has 162 nm thickness, 3.9 C/Si, 33° advancing water contact angle, 66 nm RMS roughness, and 35.8 mΩ-cm\textsuperscript{2} contact resistance. The corresponding value when pH 1 polymer solution is used are 178 nm thickness, 2.8 C/Si, 40° advancing water contact angle, 63 nm RMS roughness, and 43.7 mΩ-cm\textsuperscript{2} contact resistance.

The results of the previous paragraph are consistent with the uniformity of C/Si data in Fig. 4-2-3 for the cLBL assembled coatings as alcohol content is varied in the mixed suspension. We have previously shown that increased alcohol content substantially enhances Si adsorption from pure silica suspensions due to enhanced electrostatic attraction with the surface. In other words, the silica \(\zeta\) potential in the mixed suspension has been observed to decrease from -27 mV to -37 mV as the ethanol content is increased from 1 to 50%. Although the C/Si ratio is nearly the same for cLBL assembled coatings from suspensions having various ethanol content as seen
in Figure 4-2-1, the thickness increases with the increase of ethanol content with the same application cycles as shown in Figure 4-2-3. This indicates that ethanol impact both silica and graphite adsorption. And the impact of ethanol on graphite adsorption has been under investigating in our lab.

4.2.2 sLBL and dLBL assembly

In the case of sLBL assembly, the use of pure nanoparticle suspensions eliminates the competition nature for adsorption sites which is present during cLBL assembly and permits a significant increase in the amount of graphite deposited. This increase in the amount of graphite relative to silica will increase opportunities for graphite platelet-platelet contact and should reduce contact resistance. To contribute to this effect, the pH of the polymer suspension was also increased from 1 to 5. Whereas such a change did not have a big affect in the case of competitive adsorption, a reduction in silica coverage between alternating graphite applications is expected to enhance the opportunity for graphite platelet contact. The ethanol content of the pure silica suspension was kept at 50 volume % while pure graphite was suspended in alcohol-free media to remain consistent with the pure silica and pure graphite assembly.

For dLBL assembly, the polymer layer between graphite and silica application is removed, but rather than the competitive adsorption operative in the cLBL scheme, graphite platelets are initially deposited from a pure suspension to create a template which will direct the assembly of silica nanoparticles which are subsequently
deposited. Cationic polymer is applied after directed assembly of the silica nanoparticles to promote adsorption of the next graphite layer. The procedure is described detailed in Chapter 3. The nanoparticle suspensions for both silica and graphite are the same as those for sLBL assembly.

Figure 4-2-6. Overall coating thickness obtained from the sLBL and dLBL assembly schemes in comparison to pure silica (“Si”) and pure graphite (“Gr”) coatings.

The variation of thickness with each application cycle for the sLBL and dLBL assembly schemes is shown in Figure 4-2-6. As discussed in Chapter 3, a cycle in the case of sLBL assembly consists of a polymer layer, followed by a graphite layer, followed by another polymer layer, followed by a silica layer. In the case of dLBL assembly, each cycle consists of a polymer layer, followed by a graphite layer,
followed immediately by a silica layer. In the data discussed in this section, all pure component coatings comparisons were made using pH 5 polymer solution to maintain consistency with the sLBL and dLBL coating schemes. Assembly via both sLBL and dLBL yields coating thicknesses which vary roughly linearly with the number of cycles. The thickness per cycle for both schemes falls between that of a pure graphite bilayer (38 nm) and a pure silica bilayer (5 nm). The solid and dashed lines in Fig. 4-2-6 indicate linear fits through the pure graphite and silica coatings, respectively.

The SEM images in Figure 4-2-7 demonstrate that the dispersion of graphite platelets after the initial cycle of sLBL (Fig. 4-2-7 (a), graphite layer is under silica layer) and dLBL (Fig. 4-2-7 (b)) assembly is nearly identical to that of the initial cycle of a pure graphite coating (Figure 4-2-13). This is not unexpected as the graphite adsorption conditions are identical for all three samples. However, clear graphite/silica domain separation is visible in the dLBL coating as was the case with the cLBL coating (Fig.4-2-2 (b)). For the sLBL coating, both the raw substrate and the graphite platelets are covered by a porous layer of silica nanoparticles.

SEM images of sLBL and dLBL coating surfaces after the application of three cycles are shown in Figure 4-8. As in the case of the cLBL coating (Fig. 4-2-2 (d)), we note that the graphite platelets almost entirely coat the substrate surface after three cycles of sLBL assembly (Fig. 4-2-8 (a)). However, in the case of dLBL assembly (Fig. 4-2-8 (b)) areas where only silica is present on the substrate are still clearly evident. Such on-going domain separation during dLBL assembly suggests that the
Figure 4-2-7. SEM images at 20kX of the surface of coatings prepared using a single cycle of (a) SLBL assembly and (b) dLBL assembly.

Figure 4-2-8. SEM images at 20kX of the surface of coatings prepared using three cycles of (a) sLBL assembly and (b) dLBL assembly. A white circle is used in Fig (b) to identify an exposed graphite platelet surface.

initial layer of distinct heterogeneous domains (Fig. 4-2-7 (b)) may serve as a template which propagates through the thickness on the coating. However, due the expected random nature of the adsorption process after polymer application, we do
not expect the initial array to act as a perfect template which propagates throughout
the entire thickness of the coating. As in Fig. 4-2-2 (d), a white circle is used in Fig.
4-2-8 (b) to identify an exposed graphite platelet surface. Silica nanoparticles have
clearly deposited onto underlying graphite platelets. Nevertheless, EDS
compositional analyses do suggest a degree template propagation.

The composition of the coatings with respect to the previously defined C/Si
ratio is shown in Fig. 4-2-3 as a function of the number of cycles. We note that the
carbon content relative to silica for the sLBL and dLBL coatings is substantially
greater than that of the cLBL coatings, consistent with the competitive nature of the
adsorption process which occurs from mixed nanoparticle suspensions. In addition,
C/Si is observed in Fig. 4-2-3 to decline with each cycle for both cLBL and sLBL
assembly. Such a decline is associated with increased graphite platelet coverage of
the original substrate surface as observed Fig. 4-2-2 (d) and 4-2-8 (a) for cLBL and
sLBL assembly, respectively. In stark contrast to this behavior, C/Si remains
relatively stable and high in the case of the dLBL coatings and correlates with (albeit
crude) through-plane separation of the graphite and silica domains (Fig. 4-2-8 (b)).
The implication of this discovery is that, properly tuned to a particular system of
nanoparticles, dLBL assembly may provide an alternate route to nanowire
synthesis.¹⁹⁶

Whereas domain separation and heterogeneous array formation in the initial
and each subsequent layer prepared using dLBL assembly may be understood from ζ
potential measurements in terms of electrostatic repulsion between nanoparticles, the
source of any degree of through-plane template propagation is not clear. One explanation may be optimization of enthalpic interactions between graphite-polymer-graphite versus silica-polymer-graphite layers. Direct confirmation of such a hypothesis requires a detailed analysis of the adsorbed polymer structure within each layer and is therefore beyond the scope of the present investigation.

Figure 4-2-9. Advancing contact angle data for sLBL and dLBL assembled coatings as a function of the number of cycles.

Advancing water contact angle data for the dLBL and sLBL coatings are shown in Figure 4-2-9. The solid and dashed lines in the Figure depict data for 8
bilayers of pure graphite and pure silica LBL assembled coatings, respectively. In all cases, receding contact angles were 18° with a standard deviation of 2°. For the dLBL coatings, the advancing contact angle drops abruptly to that of pure graphite after the application of a single cycle and only slightly declines with additional cycles, despite the presence of substantial amounts of silica on the coating surface from the initial cycle (Fig. 4-2-8 (b)). The wetting behavior after three cycles is identical to that of the cLBL coatings (Table 4-2-1) and is consistent with the Johnson-Dettre wetting model for macroscopic heterogeneous surface domains. The wetting behavior of sLBL is substantially different from that of dLBL, exhibiting a gradual decline in advancing contact angle with increasing number of cycles until it becomes comparable to that of a pure silica nanoparticle coating after three cycles. Examination of Figs. 4-2-7 (a) and 4-2-8 (a) reveals that the surfaces of the sLBL coatings, unlike those prepared using cLBL and dLBL assembly, contain no fully exposed graphite platelets (although exposed portions of the graphite platelets between the silica nanoparticles are clearly evident). According to the Johnson-Dettre model, the reduction in advancing contact angle of sLBL surfaces relative to either dLBL or cLBL surfaces is a result of the observed reduction in the size of the heterogeneous surface domains. The gradual decline in advancing contact angle with increasing number of cLBL cycles observed in Fig. 4-2-9 is associated with an increase in the silica nanoparticle packing density observed in the high magnification SEM images shown in Figure 4-2-10 for one (Fig. 4-2-10 (a)) and four (Fig. 4-2-10 (b)) cycles. The silica nanoparticles are clearly evident as small
Figure 4-2-10. SEM images at 50kX of the surface of sLBL assembled coatings after (a) one cycle and (b) four cycles.

Figure 4-2-11. AFM rms roughness obtained from 20×20μm areas of sLBL and dLBL assembled coatings. Data for 8 bilayer coatings prepared from pure graphite suspensions (in water) and pure silica suspensions (in 50% ethanol) with pH5 polymer are also shown in the Figure by the solid and dashed lines, respectively.
white spheres resting on the graphite platelets which fill the entire field of view in these images.

To investigate the impact of the surface morphology of these coatings on their wetting behavior, AFM analysis of 20 x 20 micrometer areas was performed after each assembly cycle and the rms roughness data plotted as in Figure 4-2-11. The results for 8 bilayer coatings prepared from pure graphite suspensions and pure silica suspensions are also shown in the Figure by the solid and dashed lines, respectively. We note that the rms roughness after the coating surface structure is fully developed (3 cycles) is nearly identical to that of the pure graphite coating for both sLBL and dLBL assembly despite the substantially different wetting behavior observed for the three schemes. As previously noted in the analysis of cLBL assembly, surface morphology does not appear to have a significant influence on water wetting behavior for this particular system in this range of experimental conditions.

In order to better evaluate the wettability of the coated samples, the wicking test on the actually fuel cell serpentine gas-flow channels (gold substrate) was performed, as shown in Figure 4-2-12. During the test, one drop of water with the volume of about 0.02ml was dropped in the channels. Figure 4-2-12(a) showed that the water drop on the gold substrate was not expanded, indicating the hydrophobic property for gold substrate. Figure 4-2-12 (b) indicated the surface became hydrophilic when the gold substrate was coated by sLBL assembled multilayer with 8 cycles. It showed that water on coated gold substrate was fully expanded (the length was 1.3inch). The wicking test demonstrated that the bipolar plate showed high hydrophilic property
Figure 4-2-12. Wicking results for (a) bare and (b) coated gold substrate.

Figure 4-2-13. Contact resistance as a function of thickness for pure Si and Gr (solid and dashed lines, respectively) as compared to sLBL and dLBL assembled coatings. When it was coated by some multilayers, and the introduction of this kind of coating...
may be expected to remove the water produced in the fuel cell quickly enough to avoid “flooding”.

Contact resistance measurements are plotted with respect to coating thickness for dLBL and sLBL assembly and shown in Figure 4-2-13. Also included in the Figure are pure graphite coatings\textsuperscript{43} prepared using pH 5 polymer solution and silica data from coatings prepared utilizing various process conditions. The pure silica and graphite are fit by solid and dashed lines, respectively. Data from pure silica coatings prepared utilizing pH 1 polymer solution are also included in the Figure to provide comparison to a broad range of thicknesses. We first note that, in contrast to the cLBL assembled coatings, the contact resistances of the sLBL and dLBL assembled coatings are much closer to that of pure graphite than pure silica at the larger thicknesses. It is also interesting to note that dLBL and sLBL assembly yield comparable contact resistance as function of thickness. This observation suggests that, at a given thickness, graphite loading is more important to platelet-platelet contact between alternating layers in LBL assembly than particle distribution (i.e., template propagation in the case of dLBL assembly). A C/Si ratio of at least 6 for coating thickness of up to 170 nm appears sufficient to ensure substantial reduction in contact resistance of an LBL assembled coating to nearly that of a pure graphite platelet coating. For example, in the case of an 87 nm thick composite coating, the contact resistance may reduced from that obtained for pure silica nanoparticles (36 mΩ·cm\textsuperscript{2}) to 4 mΩ·cm\textsuperscript{2} while maintaining surface hydrophilicity through incorporation of graphite platelets via sLBL assembly. This is an order of magnitude
reduction in the power loss in PEM fuel cell applications.

4.2.4 Conclusions

LBL assembly from stable mixed graphite-silica nanoparticle suspensions (cLBL assembly) yields competitive adsorption and heterogeneous domain separation at each layer. Unlike SAM’s, cLBL assembly yields a coating composition substantially different from the suspension from which it was formed.

Mixed graphite-silica nanoparticle suspensions are found to yield competitive adsorption, with the more rapidly adsorbing silica particles obstructing graphite platelet access to the substrate surface. Such a competitive LBL (cLBL) assembly scheme yields composite coatings with both high electrical contact resistance (~20 mΩ/cm² at 100 nm) relative to that of pure graphite platelets and relatively poor hydrophilicity (~40° advancing contact angle) relative to that of pure silica nanoparticles.

Electrostatic repulsion between heterogeneous nanoparticles may be used to direct the formation of distinct domains within a layer during LBL assembly from pure nanoparticle suspensions as long as polymer binder is not employed between applications of the heterogeneous nanoparticles. Such a directed LBL assembly (dLBL) scheme yields heterogeneous nanoparticle arrays which may be used to as crude templates which through the thickness of a coating. This technique may provide an alternate method for nanowire formation. Graphite loading is more important to platelet-platelet contact between alternating layers in graphite-silica composite
coatings than the detailed nanoparticle distribution. Resultant coatings show improved contact resistance (~6 mΩ/cm² at 100 nm) but continued poor relative hydrophilicity (~40° advancing contact angle).

Standard LBL assembly of alternating graphite-silica nanoparticle layers with intervening cationic polymer binder (sLBL assembly) yields optimum coating performance with respect to minimizing contact resistance while maximizing surface hydrophilicity. The water wetting behavior of the resultant heterogeneous domain surface distribution may be accurately predicted using the Johnson-Dettre model of contact angle hysteresis. For a ~100 nm thick coating, the contact resistance is ~4 mΩ·cm² (nearly that of a pure graphite platelets) while maintaining an advancing contact angle of 20° (comparable to that of the pure silica nanoparticles). Such behavior represents an order of magnitude reduction in the power loss in state-of-the-art proton exchange membrane (PEM) bipolar plate fuel cell applications relative to the use of ~100 nm thick pure silica nanoparticle coatings.

Surface morphology does not appear to play as great a role on wetting as surface chemical composition for the heterogeneous nanoparticles system investigated in this study. Such a system therefore can therefore be used not only to provide practical coatings for electronics applications but also model surfaces which deconvolute the effects of surface texture from chemistry to permit the study of fundamental wetting phenomena.
Appendix

Figure 4.2.14. SEM images of the pure graphite multilayer coatings under magnification of 10kx after 1 cycle from the carbon suspension with 5wt% carbon (pH5) and a polymer solution at pH1. (The Figure is from reference 43)
4.3 Hybrid Graphite/Silica(EMS) Nanoparticle LBL Assembly on Gold

In the last chapter (Chapter 4.3), three approaches (competitive LBL, directed LBL and Standard LBL) were explored to create the composite hybrid coatings by graphite and NanoX silica nanoparticles, using the cationic polymer as the binder. In this section, the above three methods are again investigated to create composite arrays. The main differences between part 4.3 and this part are: (1) a different silica source is applied, i.e. EMS silica instead of NanoX silica. It is observed in previous work that the thin films prepared from EMS silica are much more hydrophilic than those from NanoX silica. In this work, we study whether EMS silica with larger size particles impacts nanostructure formation. (2) It is previously established that solvent had a large affect on the $\zeta$ potential (and its surface charge density) of the nanoparticles. In this work, besides ethanol, another solvent (isopropanol alcohol or IPA) in the nanoparticle suspension is applied to determine how the $\zeta$ potential alternation affects multilayer formation, and how the coating properties may be adjusted consequently. (3) The pH value for the nanoparticle suspension is increased to 7. The reason for this is to investigate the impact of decreasing the negative $\zeta$ potential for nanoparticles while not hydrolyzing cationic polymer. The increase of pH maximizes the electrostatic attraction force between cationic polymer and negatively charged nanoparticles, but also increases the solvation energy, thereby potentially inhibiting adsorption. (4) The impact salt addition in suspension on multilayer structure is also investigated. The ionic strength increases by the salt addition, and then impact on $\zeta$
4.3.1. Effect of Alcohol and pH on $\zeta$ Potential

Compared to the previous study, $\zeta$ potential measurements have been expanded to higher pH values and to include IPA. The $\zeta$ potential results are shown in Figures 4-3-1 and 4-3-2 for NanoX and EMS silica nanoparticles, respectively. Regardless of the presence of alcohol, $\zeta$ potential for NanoX silica plateaus to a minimum value at a pH between 5 and 6 shown in Figure 4-3-1, suggesting complete dissociation of available silanol groups on the nanoparticle surface. In the case of the EMS nanoparticles, the $\zeta$ potential continues to decline beyond pH 6. The result for water in Figure 4-3-2 suggests that complete dissociation occurs at a pH value between 6 and 7. An increase in ionizable surface group concentration will cause a shift in $pK_a^{197}$. At the same pH values, the lower $\zeta$ potential for the EMS nanoparticle surface relative to NanoX is also consistent with higher concentration of silanol groups in EMS particle surface when comparing Figures 4-3-1 and 4-3-2.

We note from Figures 4-3-1 and 4-3-2 that in both cases, the addition of alcohol makes the $\zeta$ potential more negative, consistent with Gouy-Chapman theory $^{197}$. The somewhat smaller dielectric constant of IPA versus EtOH shown in Table 3-1 and 3-2 does not appear to be reflected in the behavior of the $\zeta$ potential. From Figure 4-3-1 and 4-3-2, we note that the IPA $\zeta$ potential is less negative than the EtOH $\zeta$ potential, inconsistent with Gouy-Chapman Theory. This discrepancy would be ascribed to complexation of silanol groups by higher molecular weight alcohols
Figure 4-3-1. $\zeta$ potential measurements as a function of pH and alcohol type for NanoX silica.

Figure 4-3-2. $\zeta$ potential measurements as a function of pH and alcohol type for EMS silica.
(including IPA) on the basis of small shifts in the isoelectric point, as seen in Figures 4-3-1 and 4-3-2. Previous investigations \(^{114,116}\) have also observed similar difference for silica and alcohol-water mixtures.

**4.3.2 sLBL, dLBL and cLBL from EtOH based suspensions**

Figure 4-3-3 depicts the variation of total coating thickness with the number of deposition ‘cycles” prepared with three different schemes. The average and standard deviation for a minimum of three random measurements of each sample are shown. In every case, immersion time in the polymer solution and nanoparticle suspensions is 2 minutes and 10 minutes, respectively. As discussed in Chapter 4.3, the thickness contributed by the polymer layer may be negligible because the presence of nitrogen (an element unique to the polymer) could not be detected by EDS spectra.

It may be found from Figure 4-3-3 that all plots were nearly linear for the initial four deposition cycles. The bilayer thicknesses for the composite coatings may be obtained from the slopes of the best linear fits through the data points in Figure 4-3-3. The slope is nearly 30nm/cycle for all three schemes, which is much lower than silica particle size (60nm), indicating the coatings are porous. In chapter 4.1, it is also mentioned that a more porous bilayer structure is observed when the \(\zeta\) potential of the previously deposited nanoparticles is increased while the substrate is immersed in the cationic polymer suspension. The more porous structure is attributed to the less polymer adsorption due to the substrate-solvent interaction. The porous structure could also been seen from Figure 4-3-4(b). The SEM images in Figure 4-3-4 are from
cLBL assembled coatings of sequential layers obtained from mixture suspension in 50(V)% ethanol. Comparison of Figure 4-3-4(a) and 4-3-4(b) indicates that distinct domain separation between the graphite and silica nanoparticle occurs during the application of a single layer. In other words, there has no silica particles are absorbed on top of graphite. This phenomenon is very similar to the observation when NanoX silica is used, as discussed in chapter 4.2. However, unlike the observation from chapter 4.2, in which the silica nanoparticles are completely covered the substrate areas where graphite platelets have not adsorbed, there is still some area where is not covered by EMS silica or graphite nanoparticles after 1 bilayer deposition. This SEM observation is also consistent with the thickness results. These phenomena may be attributed to the high repulsion force due to the high negative ζ potential for both graphite and silica at the pH of the suspending medium. The strong repulsion forces prevent the particles absorbing closely, and prevent the silica particles absorbing on top of graphite particles. A white circle is used in Figure 4-3-4 to identify the exposed graphite platelet surface. As observed from Figure 4-3-4(c) and 4-3-4(d), some adsorption of silica nanoparticles on graphite platelets are observed only after an additional polymer layer was applied.
Figure 4-3-3. Overall coating thickness obtained from different assembly schemes.
Figure 4-3-4. SEM images at 10kx for the samples prepared through cLBL from EtOH based suspensions, (a) bare gold; (b) 1 cycle; (c) 2 cycles; (d) 4 cycles. The white cycles are used to identify the exposed graphite platelet surface and illustrate the morphological differences relative to the graphite platelet which have been deposited during the previous cycle and covered by silica nanoparticles.
Figure 4-3-5. SEM images at 10kx for the samples prepared through dLBL from EtOH based suspensions, (a) 2 cycles; (b) 4 cycles

Figure 4-3-6. SEM images at 10kx for the samples prepared through sLBL method from EtOH based suspensions, (a) 1 cycle; (b) 4 cycles
Figure 4-3-7. Carbon to silicon weight % ratio from EDS measurements for various LBL assembled coatings prepared from EtOH based suspensions.

Figure 4-3-5 and Figure 4-3-6 show the SEM images for dLBL and sLBL assembled coatings. Clear graphite-silica domain separation is visible in the dLBL coatings as is in the case with cLBL coatings (Fig.4-3-4). Such separation is clearly evident even after 4 cycles. As in chapter 4.2, such domain separation during the dLBL assembly suggests that propagation through the thickness of the coating served by the initial layer of distinct heterogeneous domains may be reached to some extent. For the sLBL coating, both the raw substrate and the graphite platelets are nearly completely covered by a porous layer of silica nanoparticles even only one bilayer
Comparison of Figure 4-3-3 to Figure 4-3-6, it may be found out that, the overall coating thickness for samples prepared by sLBL approach is mainly contributed by silica nanoparticles, while mainly by graphite platelets for dLBL method, and the cLBL scheme fell between dLBL and sLBL.

The composition of the coatings with respect to C/Si ratio is shown in Figure 4-3-7 with a function of the number of cycles. We note that the carbon content relative to silica for the dLBL coatings is greater than those of the sLBL and cLBL coatings. Unlike the observation for NanoX silica (in Chapter 4.2), which the C/Si ratio for sLBL coatings is higher than that for cLBL coatings (Figure 4-3-7), the C/Si ratio for sLBL and cLBL coatings are comparable when EMS silica was applied. This means coatings prepared from sLBL absorbed more silica nanoparticles and graphite platelets than those prepared from cLBL, and is consistent with the thickness results and SEM images (Figure 4-3-3 to Figure 4-3-6).

Figure 4-3-7 shows that C/Si ratio for cLBL assembly declines with the application of additional bilayers until a plateau is reached after 3 bilayers. Again, this result suggests that the graphite platelets are more readily adsorbed onto the bare substrate than onto previously deposited nanoparticle layers. The conclusion is consistent with our previous research. C/Si ratio for dLBL assembled coatings remains high in spite of how many bilayers application. Such behavior indicates enhanced graphite platelet association between layers and correlates with the crude through-plane separation of graphite and silica domains observed in Figure 4-3-5.
The water wetting behavior (measured by advancing contact angle) for all coatings prepared from three schemes are shown in Figure 4-3-8. In all cases, the receding contact angles are about 10º with a standard deviation about 2º. For the dLBL assembled coatings, the contact angle dropped to that of pure graphite after the application of a single cycle and only slightly declines with additional cycles, despite the presence of silica nanoparticles on the coating surface after the initial cycles (Figure 4-3-5). This result is consistent with the Johnson-Dettre wetting model for macroscopic heterogeneous surface domains126, 195. According to the theory described in Chapter 2, Cassie Equation132, 134 need be applied when the domain size decreases to some extent, this could explain the water contact angle on cLBL assembled thin films. The wetting behavior of sLBL is substantially different from that of dLBL, exhibiting a gradual decline in advancing contact angle with the increase of cycle numbers until it reaches that of a pure EMS silica nanoparticle coating after 4 cycles. This is comparable to the observation found in Chapter 4, which concluded that gradually decrease in contact angle was caused by reduction in the size of the heterogeneous surface domains and the increase of silica nanoparticle packing density. The decreased water contact angle for sLBL assembled thin films is also associated with the increased surface roughness, as seen in Figure 4-3-9. In addition to surface chemistry, the surface morphology is another important factor that affecting the wetting behavior. According to Wenzel theory131, the surface roughness may amplify the hydrophilicity or hydrophobicity, i.e. the observed contact angle should decrease with the increasing surface roughness if the contact angle on flat surface is less than 90º; and the observed
contact angle should increase with the increasing surface roughness if the true contact angle is more than 90°. As seen in Figure 4-3-9, the surface roughness for sLBL assembled coatings increased gradually and greatly with the increased application cycles. Except for the deceased domain size, the increased surface roughness is also another factor that caused the decreased water contact angle on sLBL assembled multilayers with the increased cycles. However, water contact angle for samples prepared through dLBL and cLBL schemes seem to be independent to the slightly increased surface roughness. Thus, surface morphology does not appear to play as great a role on wetting as surface chemical composition in the case of dLBL and cLBL assembly investigated in this paper.

One of the promising applications of the investigated coatings is for PEM fuel cell bipolar plates. Contact resistance of bipolar plates is a very important factor affecting fuel cell performance. High contact resistance of the bipolar plates reduces voltage output due to partial conversion to heat energy within the fuel cell. Thus, an important object in this paper is control over the coating electrical properties, especially the conductivity in the direction of vertical to the coating surface, including contact resistance and bulk resistance. Generally speaking, the contact resistance is much higher than bulk bipolar plates resistance is the investigated cases.
Figure 4-3-8. Advancing contact angle data for assembled coatings prepared by different schemes as a function of the number of cycles.

Figure 4-3-9. AFM rms roughness obtained for 20umx20um areas of assembled coatings.
Figure 4-3-10 is a plot of coating contact resistance versus application cycles prepared by the three different approaches. For all the coatings, a monotonic increase in contact resistance with cycles is observed. Compared to the pure silica coatings described in Chapter 4.1, all the coatings here own much lower contact resistance. This demonstrates that the incorporation of conductive graphite platelets could greatly decrease the contact resistance and increase the electrical conductivity. Thus, for dLBL assembled coatings, a reduction in contact resistance over pure silica may be obtained at a given application cycles, but a substantial loss in surface hydrophilicity. It may be seen from Figure 4-3-10 that the contact resistance for sLBL and cLBL assembled coatings were comparable, resulting from the comparable C/Si ratio for the coating composition, as seen in Figure 4-3-6.

The volumetric electrical through plane resistivity (i.e. the contact resistance shown in Figure 4-3-10 divided by the coating thickness seen in Figure 4-3-3) was also studied and shown in Figure 4-3-11. We note that on the case of dLBL assembly does the resistivity appear to plateau to a characteristic value of 0.08 kΩ·cm. This value is identical to that of pure graphite coatings⁴³, in spite of substantial amount of silica within the coatings. The plateau is also a sign for suggestion that a uniform coating structure has been achieved after 3 bilayers, consistent to the observation in the previous paper. However, the volumetric resistivity for other two kinds of coatings is increased with the number of cycles. Such behavior suggests a uniform coating structure has not been achieved even after the application of 4 bilayers. Similar observation is also obtained for pure silica thin films, which concluded uniform
Figure 4-3-10. Contact Resistance for assembled coatings prepared by different schemes as a function of the number of cycles.

Figure 4-3-11. Volumetric electrical through-plane resistivity associated with Figure 4-3-10.
coating structure has not been achieved even after 8 bilayers. The maximum resistivity for coatings prepared is 0.57 KΩ-cm, which is for cLBL assembled coating with 4 cycles.

4.3.3 Effect of Salt Addition on cLBL Assembled Multilayer Structure from EtOH based Suspensions

Figure 4-3-12 and 4-3-13 show the SEM images for samples prepared with cLBL approach from EtOH based suspension with or without salt. Graphite domains are more dispersed when salt is added into the mixed nanoparticle suspensions. This coincides with the decreased values of ζ potential for nanoparticles with the salt addition. From the Debye-Huckel approximation Equation (Equation 4-1, \( \zeta = -\frac{\sigma}{\varepsilon k} \)), the Debye parameter, \( k \), will be increased when the ionic strength is increased, and the salt addition greatly increases the ionic strength, thus, the absolute value of ζ potential decreases. For example, the absolute value of ζ potential for EMS silica decreases from -58.1mV to -43.3mV with the addition of 0.001 M Na₂SO₄ in suspensions containing 50% ethanol. One explanation for the enhanced dispersion is that graphite is very ready to aggregate during the LBL assembly and the reduced ζ potential would cause graphite to aggregate more readily because in our studies, both graphite and silica nanoparticles rely on electrostatic forces to stabilize the suspensions. This may explains why the graphite domains in LBL assembly prepared from suspensions with Na₂SO₄ addition are much larger than those prepared from suspensions without salt. Furthermore, the reduced ζ potential will also lead to
decrease the electrostatic interaction between the cationic polymer and graphite nanoparticle, causing the less graphite platelets to be adsorbed. Whereas these salt effects may be similar for the silica nanoparticles, the more rapid adsorption allows them to more easily compete suitable sites because of shielding when salt is present.

From the SEM images shown in Figure 4-3-12 and 4-3-13, it may be seen that the topmost graphite platelets are totally free of silica due to the repulsion force between the silica and graphite nanoparticles. However, the previously absorbed graphite particles are covered by the subsequently absorbed silica particles. From the higher resolution SEM images shown in Figure 4-3-14, silica nanoparticles were observed to nearly fully cover the graphite gaps and more silica was absorbed when the cLBL assembled coatings are prepared from suspensions with salt. This observation is consistent with the thickness data for coatings, as shown in Figure 4-3-15, and with the carbon to silicon weight ratio results, as shown in Figure 4-3-16. The coatings prepared with a without salt have comparable overall thickness, while less C/Si ratio for cLBL assembly prepared from suspensions with salt.

The results shown Figure 4-3-15 and 4-3-16 are consistent with the observation that less graphite platelets and more silica particles were absorbed with the addition of salt. From the SEM images shown previously.
Figure 4-3-12. SEM images at 10kx for the samples prepared through cLBL approach with 2 cycles from EtOH based suspensions. (a) with no salt addition; (b) with salt addition

Figure 4-3-13. SEM images at 5kx for the samples prepared through cLBL method with 4 cycles from EtOH based suspensions. (a) with no salt addition; (b) with salt addition
Figure 4-3-14. SEM images at 25kx for the samples prepared through cLBL method with 2 cycles from EtOH based suspensions. (a) with no salt addition; (b) with salt addition.

Figure 4-3-15. Overall coating thickness obtained from cLBL scheme with and without the addition of salt in ethanol based suspensions.
Figure 4-3-16 Carbon to silicon weight % ratio from EDS measurements for cLBL assembled coatings with and without Na2SO4 addition from 50% ethanol suspensions.

The wettability and electrical conductivity for the coatings are further investigated. Due to the more hydrophilic silica adsorption and less graphite adsorption for LBL assembly from suspensions with salt, the advancing contact angle is not unusual to be expected be lower (21° vs. 34°), as shown in Figure 4-3-17, and contact resistance is expected to be higher, as shown in Figure 4-3-18 and 4-3-19.
Figure 4-3-17. Advancing contact angle data for assembled coatings prepared from suspensions with and without Na$_2$SO$_4$.

Figure 4-3-18. Contact Resistance for assembled coatings prepared from suspensions with and without Na$_2$SO$_4$ assembled coatings as a function of the number of cycles.
4.3.4 dLBL and cLBL from IPA based Suspensions

The solvent dielectric constant has a big effect not only for polymer\textsuperscript{198} adsorption but also for nanoparticles\textsuperscript{43} adsorption. In this part, another kind of alcohol, isopropanol(IPA), is used to adjust the dielectric constant for nanoparticle suspensions to investigate the effect of alcohol in adsorption.

The coating thickness variation with each cycle for the cLBL and dLBL assembly prepared from suspensions containing 50% IPA with pH 7 is shown in Figure 4-3-20. As previously discussed, the polymer layer is found to contribute negligibly to the
overall coating thickness since EDS could not detect the nitrogen spectra. Assembly via both dLBL and cLBL yield thickness that vary linearly with the number of application cycles. The thickness per cycle for dLBL and cLBL schemes is 30nm/Cycle and 25nm/Cycle, respectively. From Figure 4-3-20, it may be seen that the thickness for coatings prepared by dLBL and cLBL schemes from suspension containing 50%IPA was comparable to those prepared from suspensions containing 50% ethanol (Figure 4-3-3). It may be found out from the SEM images (as will be discussed next), the thickness for dLBL assembled coatings were mainly resulting from graphite platelets, while mainly attributed by silica nanoparticles for cLBL assembled thin films.

The high resolution SEM images in Figure 4-3-21 show the dispersion of silica nanoparticles and graphite platelets after the initial cycle of cLBL and dLBL assembly. The images clearly demonstrate that dLBL assembled coating contains much more graphite platelets and less silica nanoparticles than the cLBL assembled coating. This is not unexpected since silica adsorption occurs much more quickly than graphite under competitive environment, and dLBL eliminates the competitive nature due to the sequential adsorption.

As expected, clear graphite-silica domain separation is visible for both dLBL and cLBL assembled coatings as is the cases with dLBL and cLBL coatings prepared from suspensions containing 50% ethanol, not only for EMS silica but also for NanoX silica. However, less and smaller graphite domains are observed for cLBL assembly from suspensions with 50% IPA when compared to the cLBL assemblies from
suspensions with 50% EtOH regardless of salt addition (i.e. much less graphite are adsorbed and graphite platelets distribute more widely when assembly happens in suspensions containing 50% IPA in case of cLBL), as shown in Figure 4-3-22. The SEM images in Figure 4-3-22 clearly demonstrate that the coating surface structure and composition may be easily controlled by adjusting the suspension chemistry. The anomalously less negative $\zeta$ potential with IPA instead of ethanol yields enhanced carbon nanoparticle dispersion qualitatively similar to the salt effect discussed in the previous section.

Figure 4-3-20. Overall coating thickness obtained with different coating architecture prepared from particle suspensions containing 50% IPA

![Graph showing coating thickness vs. cycles for cLBL and dLBL](image)
SEM images of cLBL and dLBL coating surface after the application of three cycles are shown in Figure 4-3-23. Again, less graphite domains are observed for cLBL assembly compared to dLBL assembly. Some silica nanoparticles adsorption on graphite platelets are observed only after an additional cationic polymer is applied for both cLBL and dLBL assemblies, and exposed graphite platelets without silica nanoparticles on their surface are still clearly seen. The white cycle in Figure 4-3-23(b) is used to identify the exposed graphite platelet surface and illustrate the morphological differences relative to the graphite platelet which have been deposited during the previous cycle and covered by silica nanoparticles.

Figure 4-3-21. SEM images at 10kx for the samples with 1 cycle prepared through (a) cLBL approach; (b) dLBL approach.
Figure 4-3-22. SEM images at 2 kX for coatings with 1 cycle prepared by cLBL assembly from different suspensions (a) 50% EtOH, (b) in 50% EtOH with salt, (c) 50% IPA. The coatings structure and composition may be readily controlled by the change of suspension chemistry.
Figure 4-3-23. SEM images at 10kx for the samples with 3 cycles prepared through (a) cLBL approach; (b) dLBL approach. The white cycle is used to identify the exposed graphite platelet surface and illustrate the morphological differences relative to the graphite platelet which have been deposited during the previous cycle and covered by silica nanoparticles.

Additional visualization of the cLBL assembled coating surface morphology was performed using AFM for the sample with two application cycles. The AFM images for this composite coating is shown in Figure 4-3-24. AFM images for pure silica coating and pure graphite coating are shown for reference. The heterogeneous structure with two distinct domains mainly contributed to silica nanoparticles or graphite platelets could clearly be seen from Figure 4-3-24(a) and (b), which are consistent with the SEM images.

SEM images at low magnification for the samples with one application cycle prepared through dLBL schemes from suspensions containing 50% ethanol and 50% IPA are presented to show the graphite platelets distribution in Figure 4-3-25. Due to the elimination of competitive nature for silica and graphite nanoparticles, the coating
Figure 4-3-24. (a) Top-view AFM image for the sample prepared by cLBL approach with 2 application cycles; (b) 3D AFM image associated with Figure 4-3-16(a); (c) Top-view AFM image for pure silica multilayer; (d) Top-view AFM image for pure graphite multilayer.
structure for dLBL assemblies seemed to be much less affected by the suspension chemistry (i.e. for assemblies happened in suspensions containing 50% ethanol or 50% IPA), when compared to cLBL assemblies.

The composition of the coatings with respect to C/Si ratio as a function of the number of cycles is shown in Figure 4-3-26. The carbon content relative to silica for dLBL coatings is greater than that of cLBL coatings, consistent with the competitive nature of the adsorption process which happens in mixed suspensions. Again, the C/Si ratio for cLBL coatings declines with the increase of each cycle. Such a decline is relative to increased graphite platelet coverage of the original substrate surface. The C/Si ratio remain high for dLBL coatings due to the crude through-plane separation of graphite and silica domains observed in Figure 4-3-23(b).
To evaluate surface energy of different materials, the contact angle of water on the surface is measured. Low contact angle is an indication of a high surface energy of a material and high surface wettability. Advancing contact angle data for the dLBL and cLBL coatings are shown in Figure 4-3-27. Compared to the bare substrate, contact angle on the coating is greatly decreased for both dLBL and cLBL assembled coatings.

The wetting behaviors for dLBL and cLBL coatings are substantially different. Advancing contact angle for cLBL coatings drops abruptly to that of pure silica coatings (~17°) after 2 application cycles. This is expected because less and much smaller graphite domains are observed for cLBL assembled coatings, as seen in Figure 4-3-22 and 4-3-25. As discussion before, the contact angle for dLBL
assembled coatings drops right away to that of pure graphite coatings after the application of a single cycle and remains nearly unchanged with additional cycles, despite the presence of substantial amounts of silica on the coatings (Figure 4-3-25(b)). The wetting behavior is consistent with the Johnson-Dettre and Cassies wetting model for heterogeneous surface domains.

Figure 4-3-27 Advancing contact angle for dLBL and cLBL coatings as a function of the number of cycles.
To investigate the impact of the surface morphology of these coatings on their wettability, AFM analysis of 20umx20um areas is performed after each assembly cycle and then the rms roughness data plots in Figure 4-3-28. It may be seen that the roughness reaches a plateau after 3 cycles for both dLBL and cLBL coatings, indicating the uniform coating is obtained. As previously discussed in the analysis of dLBL and cLBL coating prepared from suspension containing 50% ethanol, surface morphology does not appear to have a significant influence on water wetting behavior for these coatings under the range of experimental conditions.

Figure 4-3-28. rms surface roughness for cLBL and dLBL assembled coatings.
Furthermore, the wiking test on the actually fuel cell serpentine gas-flow channels is performed in order to better evaluate the wettability of the coated bipolar plates, as shown in Figure 4-3-29. The plate is coated by cLBL assembled coating with 2 cycles prepared from suspension containing graphite platelets, EMS silica nanoparticles and 50% IPA. During the test, one drop of water with the volume of about 0.02ml is dropped in the channels. Figure 4-3-29(a) shows that the water drop on the bare gold bipolar plate is not expanded, indicating the substrate is very hydrophobic. Figure 4-3-29(b) shows the wicking results on the coated bipolar plate, and the water expands to about 1.5 inch in length. As the pure silica nanoparticle coatings discussed in Chapter 4.1, the water droplet wets the coated plate nearly instantaneously (<1s). Based on this observation, it may be expected to remove the water produced in the fuel cell enough quickly to avoid water holdup.

![Figure 4-3-29. Water wicking test on (a) uncoated gold substrate and (b) coated substrate.](image)

The sample in Figure 5-22(b) was coated by cLBL assembled coating with 2 cycles prepared from suspension containing 50% IPA.
Contact resistance values for the coatings prepared by dLBL and cLBL schemes from suspensions containing 50% IPA are plotted in Figure 4-3-30 as a function of the number of cycles. The contact resistance monotonically increases with the number of cycles deposited and qualitatively corresponds to silica and graphite uptake. The contact resistance decreases a lot for cLBL coatings when compared to the pure EMS silica multilayers (Chapter 4.1) because of the introduction of conductive graphite platelets. When the contact resistance results for all cLBL assembled coatings are compared (i.e. from 50% IPA, 50% EtOH with and without salt), the contact resistance for coatings prepared from 50% IPA is mediate between the other two. This may be attributed to more porous coating structure. From Figure 4-3-16 and 4-3-26, the C/Si ratio for coatings prepared from 50% IPA and 50% EtOH with salt is comparable, indicating less graphite and less silica were absorbed for coatings from 50% IPA. The contact resistance for dLBL coatings is much closer to that of pure graphite coatings due to the rough template propagation. Again, for dLBL assembled coatings, a reduction in contact resistance over pure silica may be obtained at a given application cycles, but a substantial loss in surface hydrophilicity.

4.3.5 Conclusions

Coatings with heterogeneous structure containing silica nanoparticles and graphite platelets are successfully prepared on gold substrate by dLBL, cLBL and sLBL assembly. The paper shows that the coating structures and the corresponding
properties for the coatings may be adjusted by changing the film’s architecture and the chemistry for nanoparticle suspensions.

The coating structure and resultant properties for assembled multilayers prepared through cLBL approach from suspensions containing 50% ethanol, 50% ethanol with 0.001M Na₂SO₄, and 50% IPA are extensively investigated. Least graphite is absorbed when 50% IPA is in suspensions. The addition of salt in suspension containing 50% ethanol also decreases the graphite adsorption due to the decrease of absolute value of ζ potential for graphite, while increase the silica adsorption because of the electrostatic shielding force between silica nanoparticles. As a result, the contact angle
for coatings prepared from IPA suspensions is lowest as around 17°, coatings from EtOH suspensions is highest as 34°, and from EtOH suspensions with salt is mediate as 21°. Coatings prepared from 50% EtOH suspension has the lowest contact resistance when compared to the other two with the same application cycles, this could also be attributed to the highest graphite adsorption amount. And contact resistance for coatings prepared from 50% IPA suspensions is between those for coatings prepared from 50% EtOH with and without salt, resulting from porous coating structure.

C/Si ratio for coatings prepared by dLBL scheme from both suspensions containing 50% ethanol and 50% IPA is much higher than those prepared by other schemes, resulting in higher electrical conductivity and poor water wettability.

The sLBL involves the adsorption of silica and graphite alternatively onto the surface using polycation binder between any two layers of nanoparticles. Much silica nanoparticles are absorbed using this scheme when compared to dLBL and cLBL methods, resulting in high hydrophilicity

Surface roughness seems not to play as great role on wetting as surface chemical composition for the coatings investigated in this study. The wetting behaviors for the prepared coatings may be explained by Johnson-Dettre model and Cassie Equation.
4.4 Durability Research on Nanoparticle LBL Assembly on Gold Substrate

LBL assembly is investigated widely to prepare conformal and uniform coatings with precise and rational control over both physical (e.g. thickness, optical index) and chemical (e.g. surface energy) properties. By utilizing electrostatic forces, Van der Waals forces, hydrogen bonding or secondary interactions such as hydrophobic forces, LBL assembly can design thin films composed of polymer and other organic or inorganic materials in nano scale structures which other techniques are impossible to construct. Despite the fact that the publications about LBL assembly has increased exponentially in recent years (as seen in Figure 1-5), durability research on these kinds of thin films is, to our knowledge, rare. Cohen, et.al. reported that hydrothermal treatment of the nanoparticle coatings could greatly enhance the mechanical durability. Other methods, such as casting at high temperature, UV irradiation, are also studied to improve the as-assembled multilayers durability properties. As-assembled coatings after several dips are also found to be surprisingly robust, since the coatings could not be removed by both sonication in organic solvents and sonication in NaCl solution.

For practical application of any coating, the mechanical durability is extremely important. Coatings for PEM fuel cell bipolar plates is one of the promising applications for the nanostructured films we developed during this research, so it is necessary to know the durability requirement for fuel cells. Currently, lifetime is one of the two major challenges (cost being the other) for commercialization of PEM fuel
Automotive fuel cell systems need to be as durable and reliable as current combustion engines. Thus, the PEM fuel cells for automotive use will typically have to last for 5,000 hours (equivalent to 150,000 driven miles), and the performance loss should be less than 5% over the lifetime. As a component for fuel cells, the coatings for bipolar plates also need to reach this strict requirement. In this part of the study, the durability for the as-prepared coatings discussed in the previous chapters (Chapter 4.1–4.4) will be investigated, Due to the presence of interpenetrating materials (i.e. charged polymers) that bridge the deposited particles together within the multilayers, as-assembled nanoparticle-polymer multilayers are expected to show good durability.

### 4.4.1 The durability test for pure silica coatings

The specific polyelectrolytes employed in this study are copolymers of acrylamide and a quaternary ammonium salt, as shown in Figure 3-1. Long-term adhesion behavior of these polyelectrolytes to substrates is of concern, since the acrylamide part would be hydrolyzed to carboxylic acid under humidified fuel cell operating conditions, as seen in Figure 4-4-1. A mitigating factor is that hydrolysis will not alter the electrostatic charge density along the polymer chain in an acidic environment. Similar materials have already exhibited excellent durability in microelectronics applications.
Because cationic polymer is used as the binder for inorganic nanoparticles, it is necessary to know whether this polymer is stable or not under the durability test conditions before the durability test for all kinds of coatings. Unfortunately, instrumental analysis tools such as SEM and EDS are found incapable of detecting the polymer layer due to the atomic level thickness. ToF-SIMS is used to obtain the mass spectra for polymer coating (only one layer) prior to and after 6 days durability test, as shown in Figure 4-4-2. Compared with Figure 4-4-2(a), it may be found from Figure 4-4-2(b) that the intensity for the groups such as CN (26), CNO (42), which arise from cationic polymer, remain unchanged prior to and after durability test. This suggests that the polymer is very stable under the testing conditions. Furthermore, advancing contact angle measurement results support this finding. Table 4-4-1 shows the contact angle for the polymer coated sample before and after durability test. The results show that the contact angle decreased from 84 ° for bare substrate to 49 ° for polymer coating, and remained nearly the same after 6 days durability test.

Table 4-4-2 lists the durability results for some pure silica nanoparticle coatings on gold substrate. One coating is prepared with NanoX silica nanoparticles from
suspensions containing 50% ethanol. Another is prepared from suspensions containing EMS silica nanoparticles with no alcohol. Again, the durability test is carried out at 80°C for 6 days. Table 4-4-2 shows that almost all the adsorbed silica nanoparticles for both coatings are gone after 6 days durability test. The removal of silica nanoparticles increases the hydrophobicity.

The NanoX silica nanoparticle coatings (4 bilayers) are also applied onto industrial PEM fuel cell bipolar plates for fuel cell testing. The preparation conditions for this NanoX silica coating is the same as that shown in Table 4-4-2. However, 4 bilayers of NanoX instead of 8 bilayers are applied to minimize the electrically contact resistance. After 1461 hours running, some areas lost hydrophilicity and some did not. ToF-SIMS analysis was carried out to determine mechanism(s) for the loss of hydrophilicity. Figure 4-4-3 shows the ToF-SIMS mapping images (positive) for secondary ions obtained from the bipolar plate surfaces for both hydrophilic areas and hydrophobic areas. The areas shown in Figure 4-4-3(a) exhibit hydrophilicity while areas shown in Figure (b) ~ (d) are hydrophobic. As noticed in Figure 4-4-3(a), the silica coating remains uniform and conformal, and the silica nanoparticle coating covers the gold substrate completely as the Au map shows a very dark color. The reason for the hydrophilicity loss in the areas shown in Figure 4-4-3 (b) ~ (c) is that the hydrophilic silica nanoparticle coating is removed and becomes uneven (some areas in the Si maps shows green color), and the hydrophobic gold substrate is exposed (the Au map shows red color). The sample shown in Figure 4-4-3(d) is hydrophobic although the silica coating remains in some areas. This may be attributed to the fact that the silica
Figure 4-4-2. Negative ToF-SIMS static spectra for polymer (one layer) coated gold substrate prior to (a) and after (b) durability test. The durability test was carried out by immersing the coated substrate into 80°C water for 6 days.
Table 4-4-1  Contact angles for bare gold substrate and 1 layer polymer coated substrate

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<th>Samples</th>
<th>Advancing contact angle(º)</th>
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<tr>
<td>Bare gold substrate</td>
<td>84.4±5.0</td>
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<tr>
<td>polymer coated substrate (prior to durability test)</td>
<td>49.4±3.1</td>
</tr>
<tr>
<td>polymer coated substrate (after durability test)</td>
<td>48.8±2.9</td>
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Table 4-4-2. Durability results based on Si (wt)% for pure silica coatings before and after durability test a

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<th>Samples b</th>
<th>Polymer pH</th>
<th>Suspension pH</th>
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<th>Si(wt)% c After</th>
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<td>13.0</td>
<td>1.1</td>
</tr>
<tr>
<td>(p/EMS)&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>5</td>
<td>15.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

a. The test was carried out by immersing the coated samples in 80ºC water for 6 days

b. The NanoX silica with a concentration of 0.5wt% was mixed into aqueous solution containing 50(V)% EtOH, and the EMS silica suspension with a concentration of 4wt% contains no alcohol (i.e. pure aqueous suspension). The pH for both silica solutions were adjusted by H<sub>2</sub>SO<sub>4</sub> to 5.0.

The polymer solution has a concentration of 0.72g/l with pH value of 1.0.

c. The Si content was obtained by EDS and relative to C and Au.

d. The number represents the number of application cycles
coating was greatly damaged as deep pinholes may be clearly seen in the imaging. The pinholes lead to gold exposure. According to the Johnson-Dettre model, the advancing contact angle for heterogeneous surface is decided by the most hydrophobic area when the heterogeneous domain sizes are large.

The ToF-SIMS depth profiles for the samples associated with Figure 4-4-3 (a) and 4-4-3(b) are shown in Figure 4-4-4 (a) and 4-4-4(b), respectively. Figure 4-4-4(a) shows the Si intensity remains high at the beginning of sputter, and begins to decay after 60 seconds sputter. This indicates that there has still substantial silica coating on the surface, although the specific thickness is hard to obtain without reference and calibration for ToF-SIMS analysis. However, the Si intensity decreases dramatically at the beginning of sputtering for the sample associated with Figure 4-4-3(b), resulting from the removal of the silica coating, as shown in Figure 4-4-4(b). The depth profile results confirm that one of the reasons for hydrophilicity loss is due to the coating removal, consistent with the conclusion drawn from the data of Table 4-4-2.
Figure 4-4-3. ToF-SIMS mapping images (positive) for secondary ions obtained from the bipolar plate surfaces coated by pure NanoX silica multilayers (4 cycles) after fuel cell testing for 1461 hrs (2 months). (a): areas remain the hydrophilicity; (b)~(d): areas lost the hydrophilicity; (e) the relative concentration bar, If the black color in the mapping image (left side in the bar) means the concentration of that group or elements is very low, and if the white color (right side in the bar) means the concentration is very high. The field of view was 154×154 μm²
Figure 4-4-4. ToF-SIMS depth profile (positive) for the samples (a) associated with Figure 4-4-3(a) and (b) associated with Figure 4-4-3(b)
<table>
<thead>
<tr>
<th>Assembly scheme $^b$</th>
<th>Silica type $^c$</th>
<th>Polymer pH</th>
<th>As-prepared</th>
<th>After 6 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C (wt%)</td>
<td>Si (wt%)</td>
</tr>
<tr>
<td>(cLBL)$_4$ $^d$</td>
<td>NanoX</td>
<td>1.0</td>
<td>27.5</td>
<td>9.2</td>
</tr>
<tr>
<td>(cLBL)$_2$</td>
<td>EMS</td>
<td>4.6</td>
<td>22.1</td>
<td>3.5</td>
</tr>
<tr>
<td>(cLBL)$_4$</td>
<td>EMS</td>
<td>4.6</td>
<td>39.8</td>
<td>11.7</td>
</tr>
<tr>
<td>(dLBL)$_8$</td>
<td>NanoX</td>
<td>1</td>
<td>42.1</td>
<td>6.7</td>
</tr>
<tr>
<td>(dLBL)$_8$</td>
<td>NanoX</td>
<td>4.6</td>
<td>43.5</td>
<td>3.6</td>
</tr>
</tbody>
</table>

a. The pH for all the nanoparticle suspensions (i.e. graphite and NanoX silica mixture suspensions, graphite and EMS silica mixture suspensions, graphite suspensions, silica suspensions) was 5.0.

b. cLBL represents competitive LBL assembly, and dLBL is for directed LBL assembly. (read chapter 4 for detailed information)

c. The mixture suspensions (i.e. graphite and NanoX silica mixture, graphite and EMS mixture) used for cLBL assembly contain 50% ethanol. The silica suspension (i.e. NanoX silica suspension) used for dLBL assembly also contains 50% ethanol. The graphite suspension used for dLBL assembly contains no alcohol

d. The number means the application cycles
4.4.2 The durability test for cLBL and dLBL coatings

The durability for coatings prepared by cLBL and dLBL schemes is next investigated. Tables 4-4-3 summarizes the EDS results for three cLBL assembled coatings prepared from graphite and NanoX silica mixture suspensions or graphite and EMS silica mixture suspensions with 2 or 4 application cycles, with the mixture suspensions containing 50% ethanol. The EDS results for two dLBL assembled coatings are also depicted in Table 4-4-3. EDS results show that after 6 days durability testing in 80ºC water, the durability is no greater than that of pure silica coatings (the absorbed silica nanoparticles are almost lost, while the absorbed graphite platelets remain). This leads to increased contact angles and decreased contact resistance.

The results in chapter 4.4 show that the coatings prepared by cLBL assembly scheme from suspensions containing graphite platelets, EMS silica nanoparticles and 50% IPA exhibited very promising properties (i.e. low electrical contact resistance and low contact angle). It may be seen from Table 4-4-4 that these hybrid coatings are no more durable than pure silica coating. Since the pure silica assembly are considered as a promising coating for currently PEM fuel cell industry, the hybrid coating prepared from mixed graphite and EMS silica suspensions containing 50% IPA, which showing much lower electrical contact resistance and comparable water contact angle when compared to pure EMS silica coatings, is also applied onto industrial fuel cell bipolar plates for testing. The cLBL assembly with 2 cycles prepared from suspensions containing 50% IPA is applied on real full-size bipolar plate for PEM fuel cell. After 100 hours testing in fuel cell stacks which simulate automobile operation, the coating
retains its hydrophilicity across the entire plate. However, after 6.5 months (4661 hours) testing, most areas in the bipolar plate lost hydrophilicity.

EDS and SEM analysis are applied to investigate the mechanism for the hydrophilicity loss. From the SEM images shown in Figure 4-4-5, the graphite domains are much smaller for hydrophilic areas, while graphite tends to aggregate in hydrophobic areas.

Table 4-4-4 Durability test (EDS) for some cLBL assembled coatings prepared from suspensions containing graphite platelet, EMS silica nanoparticles and 50% IPA

<table>
<thead>
<tr>
<th>Samples</th>
<th>As-prepared</th>
<th>After 6 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C (wt%)</td>
<td>Si (wt%)</td>
</tr>
<tr>
<td>(cLBL)_2</td>
<td>10.70</td>
<td>4.19</td>
</tr>
<tr>
<td>(cLBL)_4</td>
<td>14.64</td>
<td>7.25</td>
</tr>
</tbody>
</table>

a. The cationic polymer binder has a concentration of 0.13g/l with pH value of 4.6. The mixture suspension contains 5(wt)% graphite, 2(wt)% EMS silica nanoparticles and 50% IPA with pH 7.0.
b. The carbon and silicon weight ratio was compared to O and Au elements.
Figure 4-4-5 SEM images at 600x for areas showing (a) hydrophilicity after 100 continuous hours testing in Fuel Cell stacks, and (b) hydrophobicity after 6.5 months testing.

Table 4-4-5 shows the EDS results for the two areas shown in Figure 4-4-5. From Table 4-4-5, it may be seen that the carbon content and variation for hydrophobic areas is higher than those for hydrophilic areas. This may be due to the aggregation of the carbon particles, which is consistent with SEM images. The aggregation could result from the air flux or water flux during the fuel cell operation. One promising observation from the EDS data is that substantial silica remains in the coating for hydrophobic areas under the fuel cell running conditions, once again indicating the movement of the graphite particle is responsible for loss in hydrophilicity.

4.4.3 Conclusions

The durability for multilayers containing silica nanoparticles with or without graphite platelets with the polymer binder are investigated. The durability test involves the immersion of the coated sample into 80°C D.I. water for a period of time.
Table 4-4-5 EDS results for real fuel cell bipolar plate coated by cLBL assembled coatings prepared from suspensions containing 50% IPA

<table>
<thead>
<tr>
<th>elements</th>
<th>C (wt%)</th>
<th>O (wt%)</th>
<th>Si (wt%)</th>
<th>Au (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic area</td>
<td>anode</td>
<td>13.11</td>
<td>8.27</td>
<td>1.14</td>
</tr>
<tr>
<td></td>
<td>cathode</td>
<td>18.06</td>
<td>9.76</td>
<td>2.07</td>
</tr>
<tr>
<td>Hydrophilic area</td>
<td>anode</td>
<td>9.21</td>
<td>15.03</td>
<td>2.97</td>
</tr>
<tr>
<td></td>
<td>cathode</td>
<td>9.65</td>
<td>11.80</td>
<td>2.92</td>
</tr>
</tbody>
</table>

ToF-SIMS static spectra and contact angle measurement results show that the polymer coating (1 layer) is very stable. However, the absorbed silica nanoparticles for both pure silica multilayers are lost after 6 days durability test, leading to increased contact angles. Pure NanoX silica multilayer is coated on industrial PEM fuel cell bipolar plates. After operation under simulated automotive conditions, some areas exhibit hydrophilicity while others show hydrophobicity. ToF-SIMS analysis shows that the hydrophilicity loss may be attributed to mainly two reasons: one is the uniform loss of silica coating, and another is that the silica coating was greatly damaged.

The cLBL assembled coatings from mixture suspension containing 50% ethanol is found to be unstable over the durability test. Although graphite is not removed, silica nanoparticles completely lost. The dLBL assembled coatings prepared from graphite platelets and NanoX silica nanoparticles are also found to be unstable since the silica is almost lost after 6 days durability test.
The cLBL assembled coatings from mixture suspensions containing graphite/EMS silica nanoparticles and 50% IPA are applied onto industrial fuel cell bipolar plates. The coatings maintain their hydrophilicity after 100 hours testing in fuel cell stacks, while most of the areas become hydrophobic after 4661 hours running. The hydrophilicity loss is attributed to the aggregation of graphite and loss of silica nanoparticles.
Chapter 5  Summary and Outlook

5.1 Summary

In this thesis, aqueous-based LBL assembly on gold is utilized as a versatile means to create multilayer thin films. It is demonstrated that multi-dimensional coatings exhibiting high hydrophilicity and high electrical conductivity can be created via LBL deposition of cationic polyelectrolytes and anionic nanoparticles. The conclusions based on the experiments can be summarized as following:

**Phase I.** A silica nanoparticle LBL assembly is investigated as a unique method of controlling the surface wetting properties of metallic substrates employed as bipolar plates in PEM fuel cells while maintaining a low electrical surface contact resistance. Conclusions that can be drawn from this study are:

(1) Nanoparticle adsorption occurs rapidly, with equilibration of surface coverage obtains after only 1 minute and uptake which is nearly linear with respect to the number of bilayers deposited.

(2) An increase in the absolute value of the (negative) $\zeta$ potential in NanoX silica suspension is found to increase the bilayer thickness to an average value as high as 82% of the individual nanoparticle diameter. A more porous bilayer structure is observed with larger silica EMS nanoparticles with a maximum bilayer thickness to 65% of the nanoparticle thickness.

(3) A more densely bilayer structure is observed when the $\zeta$ potential of previously deposited nanoparticle is increased while immersed in the cationic copolymer
suspension. The implication of such behavior is that copolymer and silica adsorption inhibited by substrate-solvent interaction.

(4) Wetting measurements demonstrate that silica LBL assembly results in a substantial reduction in contact angle from 84° on the bare substrate surface to as low as 7° after the application of 8 bilayers.

(5) Monotonic increase in coating contact resistance is observed with an increase in the thickness with a characteristic volumetric resistivity as low as 1.63 kΩ-cm with NanoX silica. Coatings prepared from LBL assembly of EMS silica nanoparticles have been characterized as insulators.

(6) Thickness may be increased if the difference in the oppositely charged ζ potentials of the adsorbing components is enhanced through alcohol addition (to alter the dielectric constant) at a given suspension pH. Interestingly, an opposite effect is observed if the ζ potential difference is increased through pH variation at a given dielectric constant (to alter the extent of dissociation of ionizable surface groups). This previously undocumented difference in behavior is thus for the first time associated with changes to the surface chemical heterogeneity of the nanoparticles.

Phase II. Three various LBL assembly schemes are explored to create nanostructure composite coatings containing graphite platelets and NanoX silica nanoparticles from suspensions containing various ethanol contents. Conclusions may be drawn from this study are:

(1) cLBL assembly from stable mixed graphite-silica nanoparticle suspensions
yields competitive adsorption and heterogeneous domain separation at each layer. The cLBL assembled coatings exhibit relative low hydrophilicity and low electrical conductivity.

(2) The carbon content for the composite arrays prepared by dLBL assembly scheme is notably higher than those prepared by other two methods, resulting in enhanced contact resistance but poor hydrophilicity. Such a directed LBL assembly (dLBL) scheme yields heterogeneous nanoparticle arrays which may be used to as crude templates which through the thickness of a coating.

(3) sLBL assembly of alternating graphite-silica nanoparticle layers with intervening cationic polymer binder yields optimum coating performance with respect to minimizing contact resistance while maximizing surface hydrophilicity. The water wetting behavior of the resultant heterogeneous domain surface distribution may be accurately predicted using the Johnson-Dettre model of contact angle hysteresis.

(4) Surface morphology does not appear to play as great a role on changes in wetting with surface chemical composition for the heterogeneous nanoparticles system investigated in this study.

**Phase III.** sLBL, cLBL, and dLBL assembly schemes are investigated again here to create electrically conductive and hydrophilic coatings containing graphite platelets and EMS silica nanoparticles from suspensions containing 50% ethanol with and without salts or 50% IPA. The following conclusions are revealed:

(1) C/Si ratio for coatings prepared by dLBL scheme from both suspensions
containing 50% ethanol and 50% IPA is much higher than those prepared by other two schemes, resulting in higher electrical conductivity and poor water wettability.

(2) The coating structure and resultant properties for assembled multilayers prepared through cLBL approach from suspensions containing 50% ethanol, 50% ethanol with 0.001M Na$_2$SO$_4$, and 50% IPA are extensively investigated. The nanoparticle domain size and domain distribution, and the coating properties may be easily adjusted by the change of suspension chemistry. The contact angle for coatings prepared from IPA suspensions is lowest as around 17°, coatings from EtOH suspensions is highest as 34 °, and from EtOH suspensions with salt is mediate as 21°. Coatings prepared from 50% EtOH suspension has the lowest contact resistance when compared to the other two with the same application cycles, this could also be attributed to the highest graphite adsorption amount. And contact resistance for coatings prepared from 50% IPA suspensions is between those for coatings prepared from 50% EtOH with and without salt, resulting from porous coating structure.

(3) By using sLBL scheme, more silica nanoparticles are absorbed onto the surface when compared to dLBL and cLBL methods, resulting in much higher hydrophilicity

**Phase IV.** The durability for LBL assembled coatings containing silica nanoparticles with and without graphite platelets are investigated. The results obtained support the following conclusions:

(1) ToF-SIMS static spectra and contact angle measurement results show that the
polymer binder coating is stable during the period of durability test.

(2) The pure silica coatings using either NanoX or EMS silica nanoparticles are lost after 6 days durability test, leading to increased contact angles.

(3) Pure NanoX silica multilayers are coated on industrial PEM fuel cell bipolar plates. After 1461 hours testing under actual operating conditions, some areas exhibit hydrophilicity while others show hydrophobicity. ToF-SIMS analysis indicates that the hydrophilicity loss may be attributed to the uniformity loss of silica coating or damage to the silica coating.

(4) The cLBL and dLBL assembled hybrid coatings are found to have comparable durability to the pure silica coatings. The cLBL assembled coatings from mixture suspensions containing EMS silica/graphite nanoparticles and 50% IPA are applied onto industrial bipolar plates. After 100 hours operation, hydrophilicity persists. However, most areas in the coating become hydrophobic after 4661 hours operation due to aggregation of graphite particles. This data indicates that ex-situ durability testing is substantially more aggressive than the fuel cell operating conditions, and that additional improvement in coatings durability is required.

5.2 Outlook

The following future investigations are recommended.

(1) This research has focused on gold-coated stainless steel substrates to permit contact resistance measurement without the competing effects of corrosions and because they are presently the most widely used bipolar plate materials.
However, graphite composites are still under consideration as fuel cell bipolar plates as well as many other materials, such as Ti, Al, etc. The substrate is expected to have a quantitative impact on adsorption and should be closely investigated. However, this thesis has shown that substantive control over coating nanostructure may be achieved independent of substrate.

(2) Durability of the LBL assembled nanoparticles coatings need to be improved. Despite the fact that many commercially attractive nanostructures have been demonstrated, the 5000 hrs automotive competitive durability limit has not yet reached.

(3) Improved understanding of coating loss mechanisms at the long operation times (uniform dissolution versus pinhole formation versus particle aggregation) is required to improve coating durability.

(4) Impact of nanoparticle chemical heterogeneity on multilayer formation needs closer investigation. The work in this thesis suggests the distribution of surface functional groups are critical to multilayer nanostructure formation, and that the interactions between the nanoparticles are not only dependent on electrostatic forces, but also many other bonding modes (hydrogen bonding, van der waals bonding, etc).
References


(3) EG&G Services; Parasons Inc; Science Applications Int In Fuel Cell Handbook; Morgantown: West Virginia, 2000.


(33) Angelopoulos, A. P.; Peters, S. Patent filing, **2005**.


(38) Dong, J. Notes for the Class "Fuel Cell Technology I". Spring **2006-07**.
(39) Angelopoulos, A. P. Notes for the Class "Fuel Cell Technology II". *Spring 2007-08.*


(52) Angelopoulos, A. P.; Jones, G. W.; Malek, R. W.; Marcello, H.; McKeveny, J. U.S. Patent 5,866,237, **1999**.


(69) Lee, D.; Rubner, M. F.; Cohen, R. E. All-Nanoparticle Thin-Film Coatings. *Nano Letters* 2006, 6, 2305-2312.


(122) Young, T. *Philosophical Transactions of the Royal Society* 1805, 95, 65-87.


(159) Lehn, J.; Mascal, M.; Decian, A.; Fischer, J. Molecular Recognition Directed Self-Assembly of Ordered Supramolecular Strands by Cocrystallization of


(203) Rouse, J.; Ferguson, G. Preparation of Thin Silica Films with Controlled Thickness and Tunable Refractive Index. Journal of the American Chemical Society 2003, 125, 15529-15536.


